PRACTICAL CHEMISTRY

BLACK AND CONANT

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PRACTICAL CHEMISTRY

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FLAMES OF ATOMIC HYDROGEN AT WORK WITH THE ELECTRIC WELDING ARC

A stream of hydrogen is directed into an arc between tungsten electrodes where the temperature is so high that the hydrogen molecules are dissociated in large part into free atoms. Such dissociation requires a large amount of energy and the recombination of these dissociated atoms to form hydrogen molecules again gives back that energy in a small space and produces an intensely hot flame (about 4000° C.). It is this flaming atomic hydrogen which is applied to the fusing and welding of metals.

PRACTICAL CHEMISTRY

FUNDAMENTAL FACTS AND APPLICATIONS TO MODERN LIFE

BY

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REVISED EDITION

New York
THE MACMILLAN COMPANY
1929

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Set up and electrotyped. Published May, 1920.
New and Revised edition, May, 1927. Reprinted September, 1927;
December, 1927; September, 1928 ; February, 1929.; June, 1929.

·PRINTED IN THE UNITED STATES OF AMERICA·

PREFACE

CHEMISTRY is so closely connected with many phases of modern life that almost everyone should have some knowledge of it. Its applications to the problems of industry and to those of the home and community have attracted unusual attention and interest. It plays no less important a part in the sciences of agriculture and medicine. For these reasons we believe that a knowledge of the *fundamental facts of chemistry* and an ability to use them should form a part of the equipment of our American youth.

It is generally conceded that in order to teach any subject effectively it is first necessary to arouse an interest in it. Fortunately this is an easy task in chemistry if the method of presenting the subject is not too formal and academic. We have found two ways of awakening the student's interest: first, by appealing to his love of the miraculous and dramatic; and second, by touching his curiosity concerning the things of everyday life. With this in view, we have outlined *numerous class-experiments to be done on the lecture-table*, often somewhat spectacular; and, wherever possible, we have drawn examples of *chemical phenomena from the student's daily experience*. Such applications of the facts and principles of chemistry, we believe, make the subject real and practical. A young person is not interested in the details of large manufacturing operations which he may never see, but he is curious concerning the composition and transformation of many familiar products.

It is important that the economic significance of chemistry and the allied industries be realized. To this end the idea has gradually been developed throughout the book that some of the common chemical materials, such as sulfuric acid, soda, and steel, are literally foundation stones of modern civilization.

The Industrial Chart (p. 181) helps to fix in the student's mind the coördination of a number of chemical industries.

The chemistry of the carbon compounds has been treated in a very elementary way, but at some length because so many organic substances are familiar and important. The chemistry of growing things, including the subject of fertilizers, has been considered in several places because of the importance of agriculture.

The recent startling advances in theoretical physics and chemistry have brought with them a serious problem for the teacher of an elementary course. It is impossible to present an adequate account of the principles of chemistry and leave these new developments to one side. At the same time the essential core of much of the new physics and chemistry involves so much physics and mathematics that it is hopeless to try to introduce it *in toto* into an elementary chemistry course. Furthermore, certain of the more strictly chemical aspects of the recent speculations are still regarded, even by their authors, as only working hypotheses, and few would care to present them in too simple and dogmatic a fashion.

In our attempt to bridge the gap between the old and new, we have been guided by the principle that even today in an elementary course the student is entitled to know some of the experimental facts which support our theories and hypotheses. To the extent that these facts are physical rather than chemical, the principle is admittedly difficult of application.

For example, we have developed the treatment of atomic structure gradually, leaving a consideration of sub-nuclear chemistry to the chapter on radioactivity, where the experimental facts which led to this development can be properly presented. In connection with our treatment of the ionic theory, we have particularly directed the attention of the student to the distinction between the nature of the valence forces in the hydrogen molecule and in sodium chloride. The mass of evidence which has accumulated showing the inadequacies of the

classical treatment of electrolytic dissociation of salts points to the probability of their complete ionization. We have therefore treated the material from the new simplified viewpoint.

As in the first edition, we have devoted considerable space to the periodic law and have often referred to it throughout the text. Now that the table can be satisfactorily arranged on the basis of X-ray spectra, it becomes a valuable tool, which the teacher can use with added confidence. At this point we have introduced a simple account of the new theories concerning electron arrangements in atoms since this is of undoubted value in explaining many of the regularities of the periodic table.

We are much indebted to our colleagues in the departments of physics and chemistry for various corrections and suggestions. But we are especially grateful to the numerous teachers who from their experience in the classroom with the first edition of the book have made definite and helpful suggestions for its revision. Among these teachers we would mention the following: Miss Eva B. Ammidown, Boston Teachers College; Mr. Nelson J. Anderson, Township High School, Waukegan, Ill.; Miss H. D. F. Haub, Technical High School, Oakland, Calif.; Mr. W. C. Hawes, North Central High School, Spokane, Wash.; Mr. J. C. Howard, Senior High School, Savannah, Ga.; Prof. I. J. Jenks, State Teachers College, De Kalb, Ill.; Mr. Harold C. Martin, South High School, Worcester, Mass.; Mr. John R. Montgomery, Whatcom High School, Bellingham, Wash.; Mr. H. A. Seddon, Senior High School, Springfield, Mo.; Mr. Homer Townsend, Bay Street High School, Daytona Beach, Fla. Dr. Norman D. Scott has read critically the proof and made valuable suggestions.

N. H. B.
J. B. C.

NOTE. — The directions for laboratory experiments to accompany the study of this book are printed in a separate volume.

ACKNOWLEDGMENT

We are greatly indebted to many people for assistance in securing suitable illustrations, especially to the following:

Prof. R. Adams Dutcher, Pennsylvania State College; Prof. Roger Adams, University of Illinois; Prof. Frederick G. Keyes, Massachusetts Institute of Technology; Mr. C. Neimeyer, Duluth; Mr. Harry S. Thatcher, Los Angeles.

We are also very glad to acknowledge the courtesy of many institutions and concerns in furnishing reliable data and illustrations. We would especially mention here the following:

Acheson Graphite Co.; American Engineering Co.; E. B. Badger & Sons Co.; The Barrett Co.; Bethlehem Steel Co.; Carnegie Steel Co.; Colorado Iron Works Co.; Continental Salt & Chemical Co.; Emerson Apparatus Co.; Foamite-Childs Corporation; Ford Motor Co.; General Electrical Co.; Goodyear Tire & Rubber Co.; Grinnell Automatic Sprinkler; Hood Rubber Co.; Houghton Mifflin Company for Moseley's picture from Gray, Sandifur and Hanna's *Fundamentals of Chemistry;* Walter Kidde & Co.; The Koppers Co.; National Lead Co.; The Walter E. Lummus Co.; U. S. Bureau of Mines; Oxweld Acetylene Co.; The Permutit Co.; Philadelphia Rubber Works Co.; C. C. Pierce & Co.; Raritan Copper Works; The Solvay Process Co.; Metal & Thermit Corporation; Texas Gulf Sulphur Co.; Vulcan Iron Works; Wallace & Tiernan Co.; The Warner Chemical Co.; Western Precipitation Co.

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PRACTICAL CHEMISTRY

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CHAPTER I

INTRODUCTION. CHEMICAL CHANGES

The work of a chemist — why we study chemistry — chemistry in industry — applied and pure chemistry — chemical changes in everyday life — what chemistry is about — what happens in a chemical change — how we recognize materials — characteristics of a chemical change — no change of weight in a chemical process.

Introduction

1. What is the work of a chemist? Chemistry deals with such widely different processes as the explosion of gunpowder and the digestion of food. Consequently a chemist's work covers a broad field. Almost all manufacturing operations involve one or more chemical processes. Manufacturers, therefore, have to employ chemists to see that these are carried out satisfactorily; in the same plant other chemists are often engaged in trying to improve the manufacturing methods (Fig. 1). Oftentimes the chemist is able to discover a way in which to turn a waste product of the industry into some useful and valuable material.

Soap, fertilizers, glass, paper, and ink are common materials which are made by a series of rather complicated chemical changes. Their manufacture has been much improved by the work of chemists. Explosives, dyes, and many drugs were first made in the chemical laboratory, were found to be valuable, and were then produced on a large scale.

The chemist is also often employed to determine the composition of various things. For example, he finds out whether there is any zinc, copper, or gold in a given rock and how much of each metal. He detects poison in food and drink; he measures the amount of sugar in a given beet or the amount of

Fig. 1. A chemical laboratory in the Hood Rubber Co.

valuable material in a fertilizer. Medical and biological work carried out in hospitals and special laboratories requires the assistance of many chemists.

2. Why study chemistry? Only a few of those who read this book will find their life work in the field of chemistry, but surely everyone should appreciate what chemistry is doing for the world. The recent developments in our methods of transportation and communication and in our materials and methods of building have been made possible by applied chemistry. In every household the cooking, laundering, and cleaning are also

examples of applied chemistry. In the production of our food, from the time the seed is planted to the time the finished product is distributed to the consumer, agricultural chemistry has played and will play in the years to come an important part. At present most of us are quite unconscious of the debt we owe to the chemists who guard our water supply and enforce our laws on the adulteration of foods. All of this work can be maintained and extended only when the work of the chemist is understood by an intelligent public.

3. Chemistry in industry. Not only has chemistry made possible the recent developments in the manufacture and uses of the metals, but it has also given us such comforts and luxuries as illuminating gas, gasoline, matches, dyestuffs, and many useful medicines. As our knowledge of chemistry and our ability to apply it increase, we may hope for greater economy in our industrial processes and for extensive development in new and as yet unexplored fields. Someone has said that the industrial advancement of any country can be measured by the extent and quality of its science instruction in both school and college.

4. Applied chemistry and pure chemistry. Although the application of chemistry to our industrial and social life is the part of the subject that is more easily understood, we must never forget that chemistry is primarily to be regarded as a science; that is, a search after truth whether we see any immediate use for the truth discovered or not. Even our largest industrial corporations are to-day maintaining expensive research laboratories (Fig. 2) whose primary purpose it is to extend our knowledge of pure chemistry. As our applied chemistry expands in various directions, the unsolved problems in pure chemistry multiply and call for a more fundamental knowledge of the structure of matter. Indeed, it is one of the most striking signs of the times that a scientist in one field must appreciate the achievement in related fields. The chemist to-day must be

able to follow the researches of the investigators in pure physics because the boundary line between the two sciences is almost obliterated. The biologist must keep in close touch with the

Fig. 2. A chemical laboratory in the Ford Motor plant.

latest developments in both physics and chemistry. Thus it comes about that everybody needs to understand the fundamentals of chemistry.

Chemical Changes

5. Chemical changes in everyday life. Everyone is familiar with the fact that when wood burns a great deal of heat is produced and, except for a few particles of ashes, the original wood entirely disappears. This is such a common occurrence that we do not generally appreciate its striking significance. Apparently some sort of change has taken place during the burning for we can now no longer find any of the original wood. Another

change almost as striking occurs if we allow a piece of iron, such as a rail, to lie for some time exposed to the weather. We find that it first becomes coated and then crumbles to a mass of brown powder, which we call rust. In these cases such well-known substances as wood and iron have disappeared before our very eyes. These profound changes are examples of natural processes which we call **chemical changes.** The decaying of wood, the souring of milk, the putrefaction of meat are likewise common examples of chemical change; still others are the explosion of gasoline in an automobile cylinder, the sudden burning of a flashlight powder, and the bursting of a high-explosive shell. In all these cases certain materials disappear and new ones are formed; in every instance the properties of the product of the change are plainly different from those of the original materials.

6. What happens in a chemical change? Let us now see just what happens in some cases of chemical change.

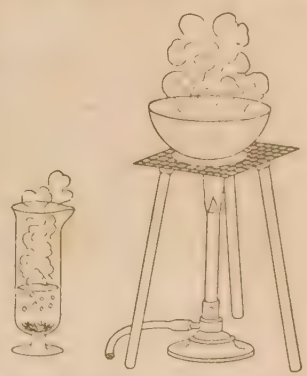


Fig. 3. Action of nitric acid on iron.

Suppose we drop a few small iron nails into a liquid called nitric acid (Fig. 3). We notice that the iron dissolves rapidly and that a cloud of brown fumes is produced. When we evaporate the solution over a flame, we find that a brown solid is left behind (Fig. 3). We can clearly see that this is not the iron with which we started. It is a new material quite different from iron.

In every chemical change one or more materials disappear and one or more new substances are formed.

If we put a solution of sugar into a glass and pour on it a little concentrated sulfuric acid,* we see a remarkable transformation (Fig. 4).

* It is convenient to use 60 grams of cane sugar dissolved in 45 cc. of water and 60 cc. of concentrated sulfuric acid.

A mass of black froth immediately appears in place of the sugar, and if we examine the black solid in this froth, we shall look in vain for our original sugar.

A little finely ground sulfur and zinc dust* may be mixed together and put in a small pile. When this mixture is touched with a flame,

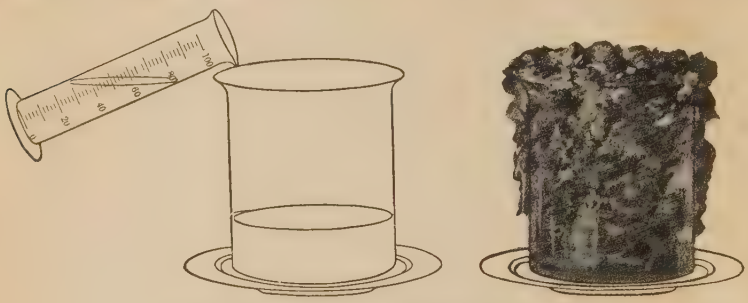


Fig. 4. Charring of sugar by sulfuric acid.

a flash at once appears and a cloud of white solid floats off. Again we find neither our original sulfur nor zinc, but only a new white substance, which is known as zinc sulfide.

In this last experiment not only was a new material formed but considerable heat and light were also produced. We usually find that **in a chemical change heat is either absorbed or evolved and light is often emitted.**

7. How we recognize materials. When we notice that ashes are different from wood and that the brown solid formed by dissolving nails in nitric acid is different from metallic iron, we are unconsciously taking advantage of our everyday knowledge of what such common materials as wood and iron are really like. No one would have any difficulty in distinguishing between a stick of wood and a bar of iron, even if the stick were painted black. Wood will readily float on water, iron will not. A magnet will attract a piece of iron but not a piece of wood. Wood easily catches fire, whereas iron will not burn. Such characteristic facts about a given material are called its

*The weight of zinc dust should be about twice that of the sulfur used.

properties. We can recognize and identify any particular material by knowing a number of these properties.

Many properties of materials can be determined accurately and expressed by numbers. For example, the weight of a unit volume of matter is called the **density** and is usually expressed *in grams per cubic centimeter*. Iron, which is heavy, has a density of about 7 g. per cc.; pine wood, being light, has a density of about 0.4 g. per cc. By determining such properties accurately we have a quick and convenient method of identifying various materials. Usually, however, it is necessary to determine several properties in order to be sure that we have completely identified the material. Other useful properties are solubility, color, melting point, and boiling point.

8. Characteristics of a chemical change. Let us take some finely divided sulfur and some iron filings.* We notice that the sulfur is a yellow powder, relatively light; it will dissolve in a liquid called carbon disulfide. The iron is a heavy, gray solid, insoluble in carbon disulfide, and readily attracted by a magnet. Let us mix these two materials together in such proportions that there is about twice as much sulfur (by volume) as iron. We place the mixture in a test tube and heat it in a flame (Fig. 5). It will be seen that in a few moments a glow spreads all through the contents of the tube, and this glow continues for a time even after the flame is removed. Evidently something has happened in the tube which has produced heat and light. If we break the test tube and examine the solid, we shall see that it is a hard, black mass. If we grind it up into small bits, we shall find that *none of it has the properties either of sulfur or of iron*. That is, none of it is soluble in carbon disulfide, and none of it is attracted by a magnet.

Fig. 5. Heating iron powder and sulfur.

In this experiment the two substances, iron and sulfur, have disappeared and a new substance, which is called iron sulfide,

* The weight of iron should be about one and three-fourths times the weight of sulfur.

has been formed. We are able to recognize these facts by carefully noting the properties of the original materials and the properties of the final product. *In a chemical change there is always a change in the properties of the materials involved.*

9. No change in weight in a chemical process. If we had carefully weighed the test tube containing the iron and sulfur before and after heating, we should have found that *no change in weight had taken place.* This is such a general and important fact in chemistry that we may very well illustrate it by another experiment.

We may select any two substances which act quickly on one another when brought together. For example, suppose we take silver nitrate and caustic-potash solutions and pour one into a short test tube and the other into a flask. We place the tube in the flask, as shown in figure 6, carefully close it, and determine its weight. Then we tilt the flask so as to bring the two clear liquids together, and we produce a dark brownish substance. The chemical change causes some rise in temperature. After the flask has cooled, we again weigh it and find that *its weight is unchanged.*

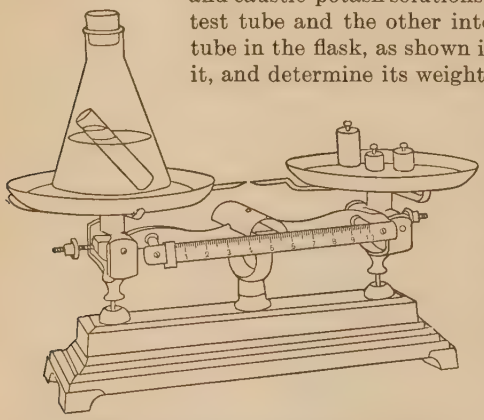


Fig. 6. Chemical change in a closed vessel; no change in weight.

A large number of such experiments have been performed with great precision, and these have shown that *in every chemical change the weight of the materials taking part in the change is exactly equal to the weight of the substances produced by the change.* This is known as the LAW OF CONSERVATION OF MATTER.

A law in science is simply a statement of some general fact which has been established by a large number of experiments. It is a description of the constant mode of behavior of certain materials under certain conditions.

SUMMARY OF CHAPTER I

CHEMISTRY deals with the composition of materials and with the changes which they may undergo.

CHEMICAL CHANGE involves a change in the identity of the material; *all* the characteristic properties disappear; one or more new materials are formed.

THE PROPERTIES of a material are the characteristics by which we identify it, such as its color, hardness, taste, density, solubility, and melting point.

HEAT and light often attend a chemical change.

LAW OF CONSERVATION OF MATTER. The weight of the materials taking part in a chemical change is exactly equal to the weight of the materials produced by the change.

QUESTIONS

1. If sand and sugar are mixed together, what property of each would you use in separating them?

2. What properties would you make use of in distinguishing between (*a*) copper wire and iron wire, (*b*) wood and iron, (*c*) aluminum and silver, (*d*) powdered sugar and flour, and (*e*) water and gasoline?

3. Name five examples of chemical change (not mentioned in the text) with which you are familiar.

4. If we pound iron it becomes hot. Have we produced a chemical change? Give your reasons.

5. If we scratch a match on a box, we produce both heat and light. Has a chemical change taken place? Give your reasons.

6. Name some property which is common to all materials.

7. Show how the Law of Conservation of Matter applies to the chemical change involved in burning coal in a stove.

8. In what ways did chemistry play an important part in the World War?

9. In what ways is chemistry of great value to agriculture?

10. How does the government make use of the chemist in the enforcement of "pure-food" laws?

11. Name five industries in which the chemist has accomplished a great saving.

CHAPTER II

ELEMENTS AND COMPOUNDS

Substances and mixtures — compounds — elements — compounds made from elements — compounds have a definite composition — mixtures and compounds compared — separation of mixtures — occurrence of the elements — number and importance of compounds.

10. Substances and mixtures. When we examine granite or ordinary concrete, we find that each material consists of more than one ingredient. Thus, in granite we find three different minerals; namely, quartz, feldspar, and mica. When the rock is crushed, these three minerals fall apart. Ordinary concrete is made by mixing together cement, sand, and crushed stone. If we examine the mixture of iron and sulfur which we used in the last chapter, we can recognize in it particles of sulfur and particles of iron. On the other hand, if we examine a mass of iron filings or a pile of powdered sulfur, we find that every particle of iron is like every other particle of iron and seems to have exactly the same properties. *A material of which every part is like every other part is said to be homogeneous* and is called by the chemist a **substance.** A material which is composed of two or more substances merely put together is called a **mixture.** Granite is therefore a mixture and not a substance. Sulfur and iron are substances which we can easily stir together to form various mixtures.

Since a substance is a homogeneous material, all parts of it will have exactly the same properties. Every sample of the substance will be found to be exactly like every other sample. On the other hand, the properties of a mixture will depend on

how much of each component is present. A mixture of 10 parts of iron and 1 part of sulfur is gray, for example, while a mixture of 10 parts of sulfur and 1 of iron is almost pure yellow.

Therefore we find that *a mixture contains two or more separate or distinct ingredients, or components, which retain their properties.*

11. Chemical compounds. Probably the most important as well as the most familiar substance is water. Yet, strange as it may seem, even pure water is not a simple substance. We may easily decompose water by an electric current into two very different substances.

We pour some water (containing a little sodium sulfate) into the apparatus shown in figure 7. The platinum electrodes are connected with a battery or generator giving at least 5 or 6 volts. The electrode in tube *A*, which is connected to the positive (+) pole, is called the **anode**, and the other electrode in *B* is the **cathode**. The current passes through the solution from the anode *A* to the cathode *B*. Small bubbles of gas are seen to rise from both electrodes, and the gas collects in *B* twice as fast as in *A*. When *B* is full we open the switch and test the collected gases. To test the gas in tube *B* we invert the tube and carefully apply a lighted match. This gas burns with a pale blue flame and is called **hydrogen**. If we invert the other tube and bring a glowing pine stick near, it bursts into flame. This gas is **oxygen**. The sodium sulfate, which was added to make the water a better conductor of electricity, is left behind in the apparatus undiminished.

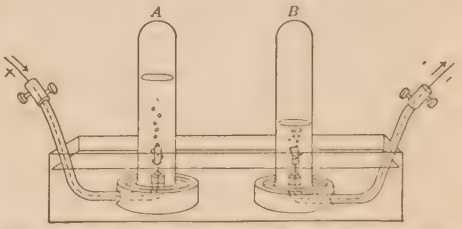


Fig. 7. Water decomposed by an electric current into oxygen and hydrogen.

Thus we see that water is decomposed by electricity into its constituent elements, hydrogen and oxygen. This process of decomposing a compound by means of an electric current is called *electrolysis*.

12. Another compound. Let us examine a red powder called **red oxide of mercury.** It is apparently a definite substance; every particle seems to be like every other particle.

We place some in a hard-glass test tube and arrange it for heating as shown in figure 8. Very soon the red powder becomes dark, and if we introduce into the tube a splinter of wood with a glowing spark on the end, the spark at once bursts into flame. This indicates that some gas, not air, is being evolved. On again examining the tube we notice that a part or all of the red powder has disappeared and that little drops of mercury (quicksilver) have collected on the sides of the tube. This forms a sort of mirror on the cooler part of the tube. If the heating is continued long enough, all the red powder eventually disappears and is converted into two products — **mercury,** the silvery liquid which is used in thermometers, and a gas which is called **oxygen.**

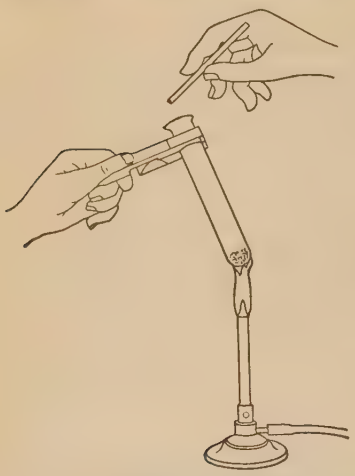


Fig. 8. Red oxide of mercury decomposed by heat.

Thus, by means of heat we have transformed a definite substance, red oxide of mercury, into two other substances, mercury and oxygen. *Any substance which can be decomposed into two or more other substances is called a* ***chemical compound.*** Hence water and red oxide of mercury are compounds.

13. What is an element? If we continue our experiments and try to produce still other substances by heating mercury, or in some other way try to decompose it, we do not succeed. Similarly, hydrogen and oxygen have never been broken down into other substances. We call such *substances which have not been decomposed into simpler substances* ***elements.*** There are more than 80 elements (list facing back cover), from which all chemical compounds are made.

It is very remarkable to find that water is composed of two gases, one of which burns and the other makes things burn much faster than air; also, that red mercury oxide is composed of a heavy silvery liquid and a colorless gas. We see that the properties of a compound are in no way like the properties of the elements of which it is made.

It was probably Robert Boyle (Fig. 9) who in 1661 first clearly defined an element. He stated that "the elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted."

Fig. 9. Robert Boyle (1626–1691). Studied effect of pressure on volumes of gases; one of the first to realize the difference between elements and compounds.

14. Compounds from elements. We shall now consider the production of a compound from two elements, the reverse of the process just discussed.

Fig. 10. Grinding mercury and iodine together in a mortar.

We place a small quantity of iodine in a mortar and pour in a little mercury. The two substances at first remain side by side unchanged; but when we rub the mixture vigorously with a pestle (Fig. 10), a red substance, quite unlike the mercury and the iodine, is formed. This is a new substance, a compound called mercury iodide.

We are all familiar with metallic copper, which has a characteristic reddish

brown color, and with sulfur, which is a brittle, yellow element. If we put some copper chips and powdered sulfur * into a small flask (Fig. 11) and heat it, the mixture begins to glow. The two elements unite with the evolution of heat and light. If we break the flask, we find a black, brittle mass which resembles neither copper nor sulfur. *The copper and sulfur have united to form a compound,* ***copper sulfide.***

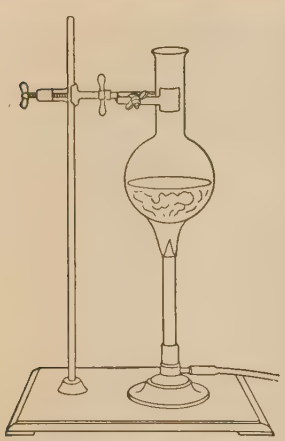


Fig. 11. Copper and sulfur heated in a flask.

Common salt is a compound composed of two elements — sodium, a bright, silvery, soft metal, and chlorine, a greenish yellow, poisonous gas. Sugar is a compound of carbon — an element with which we are familiar as charcoal — and two gases: hydrogen, which burns vigorously, and oxygen, which makes things burn furiously. In every case we find the same surprising difference between the properties of a compound and the properties of the elements of which it is composed.

15. Compounds have a definite composition. We shall find it convenient to represent chemical changes, or **reactions,** as they are often called, in a condensed form, thus:

$$\underset{(108)}{\text{mercury oxide}} \longrightarrow \underset{(100)}{\text{mercury}} + \underset{(8)}{\text{oxygen}}$$

In this *word equation* the arrow ($\longrightarrow$) is read *yield(s)*, and the plus sign (+) is read *and*. The numbers in parenthesis indicate the proportions by weight. Thus, it is found that 108 grams of mercury oxide yield 100 grams of mercury and 8 grams of oxygen.

Whatever quantity of mercury oxide is decomposed, experiments show that $\frac{100}{108}$ or 92.6 per cent of the weight used is left as mercury, and $\frac{8}{108}$ or 7.4 per cent of the weight is oxygen.

* Use about twice as much copper by weight as sulfur.

We may represent the union of copper and sulfur to form copper sulfide thus:

$$\underset{(63.6)}{\text{copper}} + \underset{(32)}{\text{sulfur}} \longrightarrow \underset{(95.6)}{\text{copper sulfide}}$$

This means that 63.6 parts by weight of copper unite with 32 parts of sulfur to form 95.6 parts of copper sulfide.

In other words, the composition of copper sulfide is $\frac{63.6}{95.6}$ or 66.5 per cent copper and $\frac{32}{95.6}$ or 33.5 per cent sulfur.

Very careful quantitative experiments show that *every pure compound has a definite composition by weight.* The whole science of chemistry is based on this fundamental fact, which is known as the LAW OF DEFINITE COMPOSITION.

16. Mixtures and compounds. The chief difference between a mixture and a compound lies in the fact that a compound has a definite composition while in a mixture the components may be in any proportion. In water, starch, sugar, and salt we have examples of compounds, each of which has a definite composition. In flour, baking powder, and the soil we have examples of mixtures, which vary in composition.

We must also remember another difference between a mixture, such as that of iron and sulfur, and a compound like iron sulfide. In the mixture we can recognize the properties of both iron and sulfur, and we find that the material is not homogeneous. In the compound iron sulfide, which we find to be homogeneous, we have an entirely different set of properties from those either of iron or of sulfur.

17. Separation of mixtures. A mixture can often be easily separated into its ingredients. For example, the iron can be attracted away from the sulfur with a magnet; the sulfur can be dissolved away from the iron in carbon disulfide, leaving the latter behind (Fig. 12). No such simple treatment as this will separate the compound iron sulfide into iron and sulfur. As a rule we can decompose a compound into its elements only

by some such drastic method as heating to a very high temperature, or passing an electric current through it.

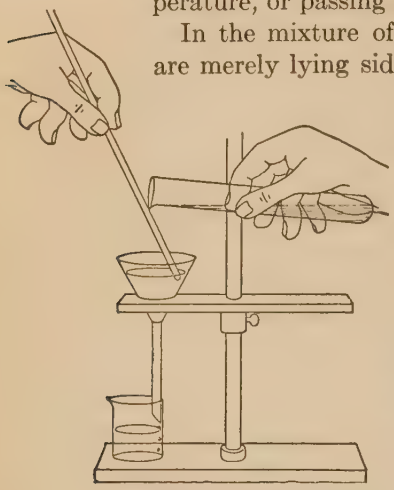


Fig. 12. Separation of iron from sulfur in solution.

In the mixture of iron and sulfur the particles are merely lying side by side. In the compound the elements are held together in chemical combination; and the result is that we have a substance entirely different from either of the original two elements.

18. Occurrence of the elements. Although there are more than 80 elements known, only about 25 of these are at all common and important. Indeed, the accompanying diagram (Fig. 13) shows that about 97 per cent of the earth's crust, including the atmosphere, is composed of only eight elements.

Most of the elements in the earth's crust occur in combination with other elements, that is, as compounds. Occasionally some elements are found uncombined, or, as it is sometimes called, in the **free** or **native state.** Copper, sulfur, and gold may be mentioned as examples of elements which are found in the native state.

For many purposes it is convenient to classify the elements into **metals** and **nonmetals.**

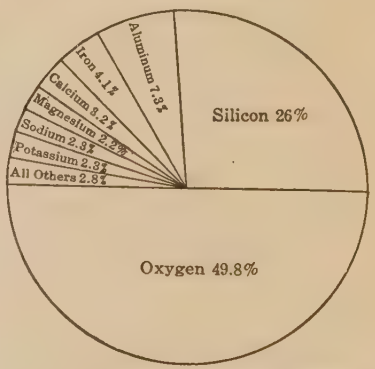


Fig. 13. Diagram showing approximately the composition of the earth's crust including the atmosphere.

Everyone is familiar with the characteristic properties of metals, such as lustre and the ability to conduct electricity and heat. Many metallic elements are common substances like iron, aluminum, silver, gold, copper, lead, zinc. The nonmetals are more varied in their properties, some being gases (oxygen, hydrogen, nitrogen) while others are solids (sulfur and carbon).

The number of elements that occur in the human body is small, and more than half of these are present in very inconsiderable amounts. The elements which are generally thought of as being essential to living plants or animals are oxygen, carbon, hydrogen, nitrogen, calcium, phosphorus, potassium, iron, and magnesium. The chemical changes which take place in living organisms are, however, very complex, and perhaps some of the other elements which occur in small quantities are equally essential.

19. Number and importance of compounds. As might be imagined, the number of compounds that can be produced by combining these eighty odd elements in different ways is very large. More than half a million are known, and new ones are being prepared and studied every day. Very fortunately only relatively few of these compounds are of importance, and therefore the study of chemistry is not so colossal a task as it otherwise would be. Moreover, as we shall see, the compounds can be divided into classes, and within these classes they are much alike. If a thorough knowledge of even a comparatively small number of compounds is obtained, the student will have a firm grasp on the fundamentals of the science.

SUMMARY OF CHAPTER II

A SUBSTANCE is homogeneous, that is, all parts are alike and show the same properties.

A MIXTURE is composed of two or more substances merely put together.

A COMPOUND is a substance which can be decomposed into two or more substances.

AN ELEMENT is a substance which has not been decomposed into other substances. Elements may be divided into metals and nonmetals.

LAW OF DEFINITE COMPOSITION: Every compound has a definite composition by weight.

COMPOUNDS	MIXTURES
Definite composition.	Components in any proportion.
In preparation, heat or light emitted or absorbed.	In preparation, no evidence of light or heat.
Can be decomposed only by chemical means.	Can often be separated by mechanical means.

QUESTIONS AND PROBLEMS

1. Careful experiments show that 7 grams of iron unite with 4 grams of sulfur. How many grams of iron sulfide will be produced?

2. State the law which is applied in Problem 1.

3. What is the percentage of iron in iron sulfide? of sulfur in iron sulfide?

4. State the law illustrated in Problem 3.

5. What element have water and red oxide of mercury in common?

6. How could you prove that sugar contains the element carbon?

7. Classify the following as elements, compounds, or mixtures: bread, milk, salt, granite, lemonade, aluminum, sugar, quicksilver, brass, and sterling silver.

8. If aluminum is more abundant than iron, give some reason why iron is cheaper.

9. Why must the list of elements be revised from time to time?

10. Write out a clear definition of the following terms as used in chemistry: *element, mixture, compound.*

TOPIC FOR FURTHER STUDY

Alchemy. The early chemists were called alchemists. What was their idea of an element? What was the principal aim of their experimentation? Did they succeed? (Moore's *History of Chemistry.*)

NOTE. *The Topics for Further Study* will often suggest collateral reading in the history of chemistry, and the application of chemistry to industry and everyday life. A list of suggested reference books will be found in the Appendix.

CHAPTER III

OXYGEN. COMBUSTION. OZONE

Importance of oxygen — preparation — test — characteristics. Lavoisier's experiments on combustion — products of combustion — oxidation — speed of oxidation — spontaneous combustion — explosions — kindling point — fire extinguishers — commercial uses of oxygen. Ozone.

20. Importance of oxygen. In our study of the elements we shall begin with oxygen. We have already met this substance as a constituent of water and of red oxide of mercury and have learned that it is the most widespread and abundant of the elements. We shall soon see that it is found in many rocks and minerals, such as sandstone and limestone, where it is combined with a great variety of other elements. Oxygen is the most active element in the atmosphere. Without it we suffocate and life is impossible. It is necessary for the production of heat from fuel since wood, coal, and gas will not burn without it; and for light wherever oil or gas is used in lamps. Thus we see that on account of its great abundance, wide occurrence, and chemical activity, it is appropriate to begin the systematic study of the elements with oxygen.

21. Preparation of oxygen. In 1774 an English chemist, Joseph Priestley (Fig. 14), prepared oxygen exactly as we did in Chapter II by heating red oxide of mercury. At about the same time a Swedish apothecary, Scheele, also prepared oxygen by this method. In fact, the latter's discovery of oxygen probably antedates Priestley's, but the results were not made public until a few years later.

In the laboratory it is more convenient to heat a compound called **potassium chlorate,** which is a substance used in medicine and in making matches and fireworks. It is much cheaper than the oxide of mercury and gives, when heated, a far larger proportion of oxygen. Potassium chlorate is a white crystalline solid, a compound of the three elements potassium, chlorine, and oxygen. When it is heated to the right temperature (360° C.)*, it melts; and, as the temperature rises still higher, bubbles of oxygen appear, leaving behind another compound of potassium and chlorine called potassium chloride. We can express this change in the following way:

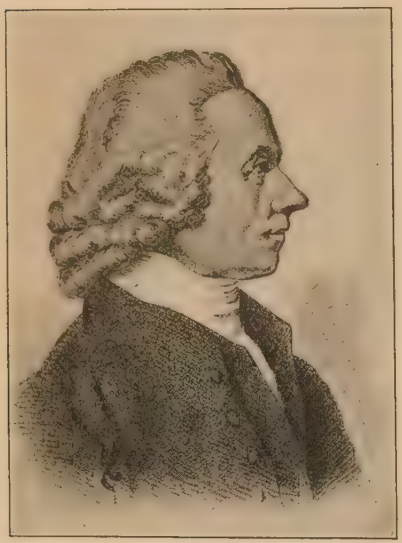


Fig. 14. Joseph Priestley (1733–1804). An English clergyman who discovered oxygen. He spent his last years in Pennsylvania.

potassium chlorate $\longrightarrow$ potassium chloride + oxygen

[potassium, chlorine, oxygen] [potassium, chlorine]

If we carefully heat some potassium chlorate in a test tube until it just melts and thrust a glowing spark into the test tube, we find that no oxygen is being evolved. We now drop a little black powder called **manganese dioxide** into the tube and test it again for oxygen. In spite of the fact that the tube has been slowly cooling down, oxygen is now produced. The manganese dioxide undergoes no change in this process.

A material which thus aids chemical action without being itself permanently altered is called a **catalytic agent** or a **catalyst.**

* The centigrade scale (C.) is commonly used in chemistry.

We shall see that catalysis plays an important rôle in chemistry, for by means of it processes may be carried out rapidly. This results in reducing the cost of operating many industries.

22. Some experiments with oxygen. In order to study the properties of oxygen, we shall need to have it in considerable quantity.

We may make it by mixing 4 parts by weight of potassium chlorate with 1 part of manganese dioxide and placing this in a thin-glass flask arranged with a delivery tube (Fig. 15). The gas is collected in wide-mouthed bottles which have been previously filled with water and inverted in the **pneumatic trough.** When the flask is gently heated, the oxygen escapes through the tube and bubbles up through the water into the bottles. The flame under the flask should be removed from time to time in order that the gas may not be too rapidly evolved and burst the flask.

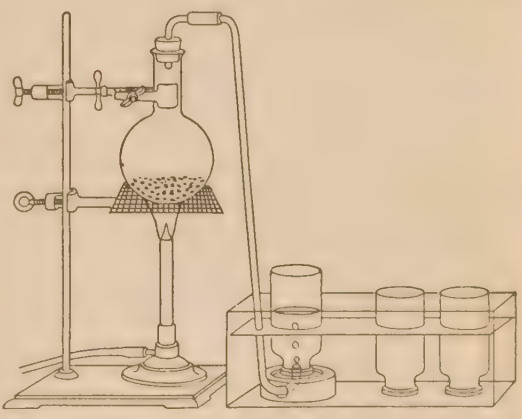


Fig. 15. Oxygen made by heating potassium chlorate and manganese dioxide.

We shall first of all convince ourselves that we have oxygen. We perform the same experiment as before (§ 12), that is, we thrust a splinter of wood with a glowing spark at one end into a bottle of the gas. The fact that the splinter bursts into flame is used as a **test** for oxygen since there is only one other gas (nitrous oxide) which behaves similarly. In general, *a distinctive property by which we commonly recognize a substance is called a* ***test.***

We shall now study the behavior of various substances when heated in oxygen.

Charcoal: We wrap a piece of copper wire around a small bit of charcoal, heat it, and then plunge it into a bottle of oxygen; it bursts into a brilliant flame.

Sulfur: We place a bit of sulfur in an iron spoon (deflagrating spoon) and ignite it by holding it for a moment in a flame. It burns with a pale blue flame, but when put into oxygen it burns with a very brilliant light.

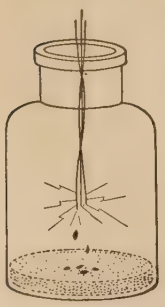


Fig. 16. Burning iron in oxygen with a shower of sparks.

Iron: It is possible to burn iron in oxygen if we use iron ribbon, such as a watch spring, or iron wire, such as a bunch of braided picture wire. First we coat the end with sulfur, then ignite the sulfur, and suspend the wire in a bottle of oxygen. The sulfur continues to burn, producing a very intense heat, which is sufficient to ignite the iron. As the iron burns it sends off a shower of brilliant sparks (Fig. 16). (It is well to cover the bottom of the bottle with a layer of sand.)

Phosphorus: This is a soft, yellow substance which may take fire even at ordinary temperatures. For this reason it is always kept under water when stored. A small bit placed in a deflagrating spoon and ignited will burst into flame when placed in oxygen. The flame is so vigorous and the light so intense that one cannot look at it with comfort. The white clouds which appear are the product of the chemical reaction.

23. Characteristics of oxygen. From such experiments as these we see that its most noticeable characteristic is this: that *substances which burn in air will burn in oxygen more rapidly and with increased brilliancy.* It is a colorless gas and is so slightly soluble in water that we have no difficulty in collecting it over water. When the gas is pure, it has neither smell nor taste and is slightly heavier than air.

Such characteristics of a substance describe its behavior and are often called the **chemical properties** of the substance. The mere name of a particular material tells us nothing; it is only when we know its properties that we are acquainted with it. Chemical substances are like individuals in this respect: if we

know only a man's name, we know very little about him. When we have learned something about his actions and character, we can tell what sort of person he is. The chemical properties of a substance describe the character of that particular kind of inanimate matter.

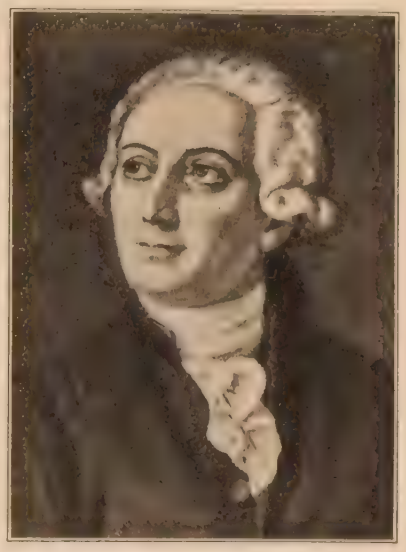


Fig. 17. Antoine Laurent Lavoisier (1743–1794). A French chemist whose work laid the foundation of modern chemistry.

24. What is "burning"? We have just seen that various substances burn more rapidly in oxygen than in the atmosphere, and so we may reasonably conclude that oxygen plays an important part in the process of burning, or combustion. This is such an important chemical change that it will repay us to examine the process with considerable care and to recall in this connection some of the early experiments.

25. Lavoisier's experiment on combustion. Lavoisier (Fig. 17) was a famous French chemist who lived about 150 years ago. He is sometimes called the "father of modern chemistry" because he discovered the correct explanation of the process of burning.

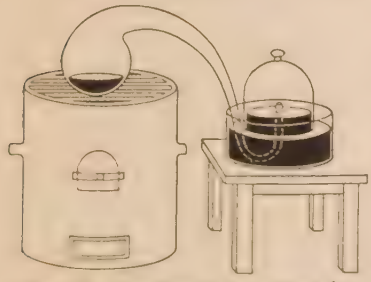


Fig. 18. Lavoisier's apparatus for studying combustion.

He heated some mercury in a retort (Fig. 18), the neck of which extended into a jar standing in a larger dish of mercury. After heating the mercury nearly to its boiling point for several days, he discovered

that *the air inclosed within the retort and jar had lost* ***one-fifth*** *of its volume.* On examining the residual air he found that a lighted splint would not burn in it but was extinguished. The material in air which enables a substance to burn had evidently been removed. In the retort he found on the surface of the mercury some red powder having all the properties of the red oxide of mercury which Priestley had used for preparing oxygen.

Lavoisier now placed this in a suitable apparatus, heated it strongly, and collected the gas evolved. He obtained a gas whose volume exactly corresponded with the shrinkage undergone by the inclosed air, and in this gas substances burned with great vigor. There was now no doubt that one-fifth of the air was composed of this gas, which *Lavoisier named oxygen.* By mixing the rest of the air left in the first experiment with enough oxygen to bring it back to its original volume, Lavoisier produced a gas having all the properties of ordinary air. Thus he proved that the oxygen of the air is the only gas used up in the process of burning.

26. Products formed by burning. But if burning is a chemical reaction between oxygen and the substances burned, what about the compounds formed by the change? What has happened to them? A candle disappears almost completely when it burns. The products of the combustion in this case are gases like oxygen itself and are invisible; they can, however, be collected and weighed. When a candle burns, the compounds formed are water vapor and a gas called carbon dioxide. These so-called *products of combustion* may be absorbed by a substance known as sodium hydroxide.

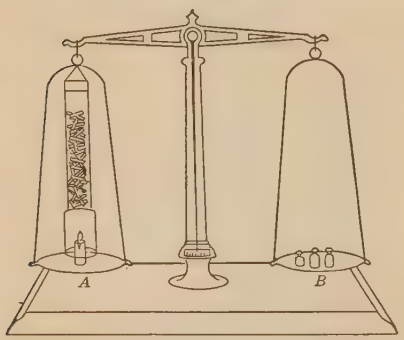


Fig. 19. The products formed by burning a candle weigh more than the candle.

If we arrange a candle on a balance pan *A* and suspend above it a tube filled with sodium hydroxide, we shall be in a position to weigh both the candle and the products of combustion (Fig. 19). We carefully balance the scales by putting suitable weights on pan *B*. We

then light the candle and notice that as the combustion proceeds pan *A becomes heavier*, although the candle is visibly disappearing. The substances produced by the burning are *heavier* than the candle which is burned. This is because they contain the element oxygen taken from the air in addition to the elements already present in the candle.

This experiment shows that *if we weigh the products of combustion we always find them to be* **heavier** *than the substance burned.* Another experiment which illustrates the same important point is as follows:

We place some iron powder in a crucible and carefully counterpoise it on a balance with the aid of weights or small shot. We remove the crucible from the pan and heat it with a flame. The mass begins to glow, showing that a chemical change is taking place. We continue the heating for about five minutes and then cool and examine the material. The crucible is found to contain a new reddish solid resembling iron rust. When the crucible is now placed on the balance pan, we find that it has gained a great deal in weight. Again the increase in weight is due to the oxygen from the air which has combined with the iron to form a new compound containing the two elements iron and oxygen.

These experiments show that when a substance burns in air, new compounds are formed by the combination of the combustible materials with the oxygen. These new compounds weigh more than the original material because they contain oxygen in addition to the combustible substances. In the case of iron the product is called iron oxide; we can represent the change as follows:

$$\text{iron} + \text{oxygen} \longrightarrow \text{iron oxide}$$

An oxide is a compound of an element and oxygen. When substances burn in air or oxygen, oxides are always formed.

27. Oxidation. The reaction of a substance with oxygen is called oxidation. When this reaction proceeds so rapidly that heat and light are produced, we call the change burning, or **combustion.** Familiar examples of oxidation are the burning of coal, wood, gas, or oil, which takes place so rapidly that

we have combustion. There are many cases of oxidation in which the change goes on so slowly that no apparent heat or light is produced. One of the best examples of this is the rusting of iron. When iron is left in contact with the atmosphere, it slowly turns into iron oxide, or, as it is commonly called, " rust." This process is hastened by the presence of water. The rusting of iron is thus exactly like the burning of wood, except that in the case of iron the change takes place so slowly that no heat effect is apparent.

28. Speed of oxidation. Different substances oxidize at very different speeds. Although combustible materials combine with oxygen at all temperatures, yet in every case the speed is increased by raising the temperature. In fact, experience shows that *in every chemical change raising the temperature hastens the process.* Some substances, like phosphorus, oxidize so rapidly at temperatures only slightly higher than normal that they take fire on merely being exposed to the air. This is well illustrated by the following experiment:

Fig. 20. Spontaneous combustion of phosphorus.

Let us dissolve a little phosphorus in carbon disulfide and pour a few drops of this solution on a piece of filter paper supported on a tripod. When the solvent evaporates, the phosphorus is left widely distributed over the paper, and every particle comes in contact with the air. Then the whole mass bursts into flames (Fig. 20). Under these conditions combustion starts at room temperature.

29. Spontaneous combustion. This experiment with phosphorus very well illustrates what occurs in so-called **spontaneous combustion.** Rags soaked with oils sometimes take fire when left lying about instead of being placed in a closed metal can. This is because a slow oxidation of the oil takes place

on the large surface exposed to the air. The rags are poor conductors, and so the heat developed finally sets the mass on fire.

30. Explosions. When certain gases — such as gasoline vapor or illuminating gas — or very finely divided combustible matter — such as coal dust or flour — are mixed with the proper proportions of air or oxygen, they will explode if the mixture is ignited by a spark. An explosion is caused by the extremely rapid combustion of these gaseous mixtures or of dust suspended in the air. Such terrific explosions have occurred in flour mills and other factories that many modern mills are now equipped with dust-removing apparatus and with devices for preventing sparks due to static electricity. In a later chapter (XXI) we shall discuss explosions due to the breaking down of unstable nitrogen compounds, such as nitroglycerin.

31. Kindling point. The other extreme is represented by iron. In order to cause this substance to burn rapidly, it is necessary first to get it into a finely divided condition, then to raise it to a high temperature, and to put it into pure oxygen. We did this in a previous experiment by coating a bundle of iron wires with sulfur and bringing it to the proper temperature by the heat evolved through the rapid combustion of the sulfur in pure oxygen; under these conditions the iron itself finally caught fire and burned.

We are all familiar with the fact that coal can be made to burn only by first building a wood fire, and that the wood must in turn be ignited by paper, which again is lighted with a match. In this series, the burning of each material raises the temperature of the next until it in turn finally "catches fire" and burns. The temperature at which a particular material will "catch fire" in air is sometimes called the **kindling point.** But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire because it presents relatively more surface to the air. Beside the physical condition of the

solid, the pressure of the surrounding air and the presence or absence of a catalytic agent also determine the temperature of ignition. In other words, there are several conditions which affect the kindling point.

One may burn a little gasoline in an open dish without danger; but a mixture of gasoline vapor and air may burn so quickly that it causes an explosion. Therefore *it is very important not to use such liquids as gasoline near an open flame*, since they evaporate rapidly and the vapor with air forms an explosive mixture.

32. Extinguishing fire. When we wish to put out a fire, we try to cool the burning material below its kindling point by pouring water on it. This usually succeeds if we have sufficient water at hand. *All methods of extinguishing fire depend either upon cooling the combustible material or upon excluding the air so that oxygen is no longer available for the oxidation.* When we use water we combine the two advantages, although water acts chiefly by cooling the burning material. Sand and gravel, which are used to extinguish certain kinds of fires, such as burning gasoline, simply smother the fire by excluding the air. So-called chemical fire extinguishers, as we shall see in Chapter VI, combine the cooling effect of a liquid with the smothering effect of a heavy non-combustible gas, which hangs like a cloud over the burning material and excludes the air.

33. Commercial uses of oxygen. The oxygen of commerce is now usually made from **liquid air,** which will be described in section 81. The liquid oxygen boils at $-182.4°$ C., but the nitrogen boils at even a lower temperature ($-194°$ C.). Therefore the latter evaporates more freely than does the oxygen. When the liquid is almost pure oxygen (about 96 per cent), the gas is pumped into steel cylinders. Physicians sometimes use oxygen for patients who are suffering from pneumonia or suffocation. It is also used instead of air when intense heat is required, as in the acetylene torch and in the oxyhydrogen blowpipe for welding metals. It is commonly employed in burn-

ing out the carbon from automobile cylinders. Oxygen in tanks is used to restore the supply in the atmosphere of submarine boats and in tunnelling. It has recently been found that the aviators who ascend to high altitudes, such as 19,000 feet, where the air is rarefied, get only half the usual amount of oxygen and so become "dopey." An equipment has therefore been de-

Fig. 21. Miners use oxygen helmets in the presence of poisonous gases.

signed to supply the needed oxygen from a tank through a connecting tube to a face mask covering the mouth and nose. All military airplanes flying over an altitude of 10,000 feet are now equipped for the use of artificial oxygen. Similar apparatus is employed in fighting mine fires and in rescuing miners trapped by poisonous gases (Fig. 21).

34. Ozone. When electric sparks pass through air or oxygen, a peculiar odor is noticed. On further study this is found to be due to a more active form of oxygen, which is called **ozone.** In

the apparatus shown in figure 22, only about 7 per cent of the oxygen can be converted into ozone. Its formation from oxygen involves an absorption of energy; and conversely, when it passes back into oxygen, it gives out energy. This action may be expressed thus:

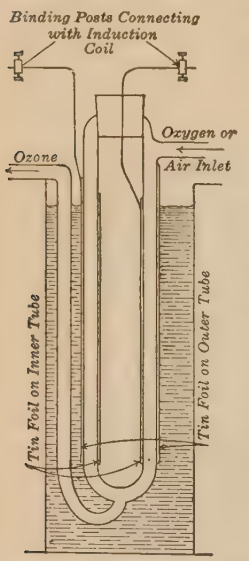


Fig. 22. Ozone generator.

$$\text{oxygen} + \text{energy} \rightleftharpoons \text{ozone}$$

Different forms of the same element which differ in their energy content are called **allotropic forms,** and the unstable form (in this case the ozone) tends to pass into the more stable form (oxygen) with the evolution of energy.

Ozone is heavier than oxygen and considerably more soluble in water. It is a much more active oxidizing agent than oxygen at ordinary temperatures. Since it oxidizes many organic compounds, it is a bleaching agent. In several large European cities it has been used to disinfect the water supply. It has been suggested as a means of purifying the air in houses and large halls, but has not given very successful results. It is a deodorizer but has very slight disinfecting action in the air.

SUMMARY OF CHAPTER III

OXYGEN CAN BE PREPARED BY:

(*a*) heating red oxide of mercury (historic);
(*b*) heating potassium chlorate (laboratory);
(*c*) evaporating liquid air (commercial).

A CATALYST is a substance which is not itself altered but which causes a chemical change to take place more easily. The addition of manganese dioxide to potassium chlorate makes the oxygen come off at a lower temperature.

OXYGEN is a colorless, odorless gas somewhat heavier than air. It combines with nearly all other elements.

OXYGEN IS USED COMMERCIALLY for the production of heat and light, for the melting, cutting, and welding of metals, and in breathing apparatus used by aviators and in mines.

OXIDATION is the process of combining a substance with oxygen.

AN OXIDE is a compound of oxygen and another element. Oxides are formed when an element burns in oxygen or air.

COMBUSTION is a chemical action in which heat and light are produced.

ORDINARY BURNING is a rapid oxidation which is accompanied by heat and light.

AN EXPLOSION is due to the very rapid combustion of certain mixtures of gases or of dust, such as coal or flour, and a gas.

THE KINDLING POINT of a material is the lowest temperature at which it takes fire and burns.

SPONTANEOUS COMBUSTION occurs when material is raised to its kindling point by the heat produced through a slow oxidation which starts at ordinary temperatures.

THE SPEED of all chemical changes is increased by raising the temperature.

OZONE is an allotropic form of oxygen produced by the action of a silent electric discharge. It is unstable and is a powerful oxidizing agent. It is used in some places for purifying the water supply.

QUESTIONS

1. Name three metals which do not oxidize.

2. How could you prove experimentally that part of the air disappears in the rusting of iron?

3. Assume that potassium chlorate is 39% oxygen. If 12 grams of potassium chlorate and 3 grams of manganese dioxide are used to produce oxygen, how much of each product is left in the flask?

4. Explain why wood in the form of shavings burns more rapidly than the same wood in the form of a log.

5. Would oxygen burn in an atmosphere of illuminating gas?

6. Why does coal packed closely in poorly ventilated bunkers often take fire?

7. Why is oxygen sometimes called a *supporter* of combustion?

8. When metals tarnish or rust, do they change in weight?

9. Why does a good draft make a fire burn more rapidly?

10. Why does blowing extinguish a candle?

11. What is the danger in letting the wind blow out a gas flame?

12. Why do we not fill balloons with oxygen?

13. How would you distinguish a bottle of oxygen from a bottle of air?

14. How would you prove that ordinary tap water contains dissolved oxygen?

15. What is the safe way to dispose of greasy cloths?

16. If your clothing caught on fire, how would you put it out?

17. Why do firemen and miners use oxygen helmets?

18. Why are buildings sometimes dynamited to stop a conflagration?

19. Name three cases of practically instantaneous combustion.

20. When the air in a mine is filled with coal dust, why does a flame often cause an explosion?

Topics for Further Study

Fire prevention. The loss of life and property by fire is a very serious matter in the modern world. State and municipal governments have passed laws tending to prevent the outbreak of fire. What are the "fire laws" in your community? What means are provided for extinguishing fires? What are the relative advantages of different kinds of fire-fighting apparatus, such as the "hand engine," the "steamer," the "chemical engine," and a high-pressure system? What are the modern methods of fireproof construction? What are automatic extinguishers?

Early American chemists. Why is the life of Priestley of especial interest to Americans? Who were some of the early American chemists, and what did they accomplish? (Moore's *History of Chemistry* and Smith's *Chemistry in America*.)

CHAPTER IV

HYDROGEN AND ITS USES

Occurrence — preparation from water and acids — displacement — purification — experiments to illustrate its properties — chemical behavior — reducing action — uses. Diffusion. The kinetic-molecular theory.

35. Where hydrogen is found. We have just studied one of the elements in water — oxygen; in this chapter we shall deal with the other element — hydrogen. This element is also a gas, but unlike oxygen it does not occur to any extent in a free state in nature. It is found in small amounts as one of the constituents of natural gas, an inflammable mixture of gases which issues from the ground in certain parts of the world. Nearly three-fourths of the illuminating gas used in this country is water gas, which is about 38 per cent hydrogen. It is also present in combination with other elements in plants, animals, and in the human body.

Fig. 23. Henry Cavendish (1731–1810). An Englishman of wealth who lived as a recluse, devoting his time to chemical research.

It was in 1766 that Henry Cavendish (Fig. 23) established the fact that hydro-

gen is an element, and a little later he proved that water is the sole product when hydrogen burns. But it was Lavoisier who in 1783 named the element hydrogen (water producer).

36. Preparation from water. We have already (§ 26) seen that iron, when heated to a moderately high temperature, combines with oxygen. If we heat iron wire red-hot in a porcelain or iron tube and then pass steam through the tube, the hot iron combines with the oxygen in the steam, setting free the hydrogen, which may be collected. The chemical change involved in this experiment may be represented as follows:

$$\text{iron} + \underset{[\text{hydrogen}\ \text{oxygen}]}{\text{water}} \longrightarrow \text{hydrogen} + \underset{[\text{iron}\ \text{oxygen}]}{\text{iron oxide}}$$

Hydrogen can be obtained from water even at ordinary temperatures by means of certain metals. Thus, if a small bit of metallic sodium is dropped on water, action begins at once. The metal is very light and runs hissing about on the surface of the water. As the action often ends with a slight explosion, a glass plate should be held up to protect the eyes. We may collect the hydrogen which is evolved by the action of sodium on water as follows:

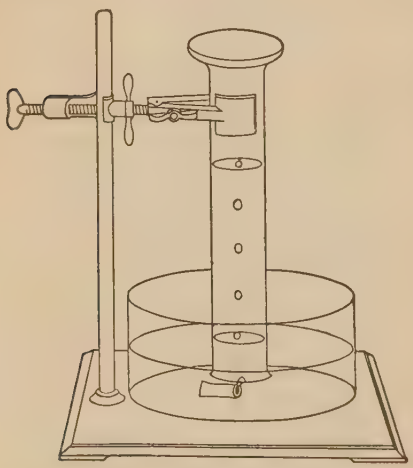


Fig. 24. Metallic sodium in water generates hydrogen.

Let us take a short piece of lead pipe (about 1 inch long and of $\frac{1}{4}$-inch bore) with one end hammered together, and fill it with freshly cut sodium. If we drop this tube with its charge of sodium into a dish of water, bubbles rise and may be collected in an inverted cylinder filled with water (Fig. 24).

If potassium is used, the action is more violent and so much heat is generated that the hydrogen is set on fire. When calcium is used, the metal sinks to the bottom of the vessel so that a bottle filled with water can easily be inverted over the metal to collect the gas as it is formed. In each of these cases *the metal displaces only one-half of the hydrogen in the water;* it combines with the remaining half and with all of the oxygen to form the compound known as the **hydroxide** of the given metal. The chemical reaction of sodium and water may be expressed thus:

$$\text{sodium} + \underset{\left[\begin{smallmatrix}\text{hydrogen}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\left[\begin{smallmatrix}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{sodium hydroxide}}$$

The sodium hydroxide and potassium hydroxide are very soluble in water, but most of the calcium hydroxide is not dissolved and may be seen suspended in the water.

37. Action of metals on acids. The most convenient way of preparing hydrogen in the laboratory is by the action of certain metals on acids. Acids are compounds which contain hydrogen and have certain peculiar properties, which we shall consider in another chapter. The commonest acid is **sulfuric,** often called "oil of vitriol." It is a heavy liquid which mixes with water in all proportions. The pure liquid is known as **concentrated** sulfuric acid; the dilute acid may be prepared by slowly pouring the concentrated sulfuric acid into four or five times its volume of water. Dilute sulfuric acid reacts vigorously with commercial granulated zinc, producing hydrogen. If the zinc and the acid are pure, the action is very slow and must be catalyzed by adding a little copper sulfate solution to the acid.

The zinc is placed in a bottle fitted with a two-hole stopper (Fig. 25). A long thistle tube (*T*) reaches to the bottom of the bottle and is used to introduce the acid and also as a safety tube. The other tube serves to conduct the hydrogen through the tube into the pneumatic trough.

After the apparatus is assembled the acid is poured through the thistle tube and the action starts at once; a copious stream of gas bubbles through the pneumatic trough and may be collected in bottles (*H*).

The reaction which takes place in this case may be represented as follows:

$$\text{zinc} + \underset{\left[\begin{smallmatrix}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{sulfuric acid}} \longrightarrow \text{hydrogen} + \underset{\left[\begin{smallmatrix}\text{zinc}\\ \text{sulfur}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{zinc sulfate}}$$

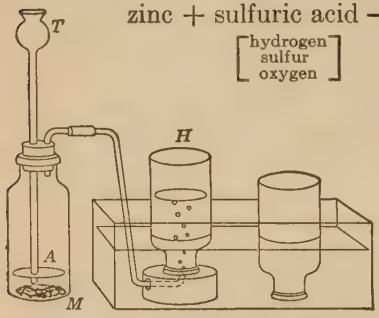


Fig. 25. Apparatus for generating hydrogen by the action of an acid on zinc.

The other product of the reaction, zinc sulfate, is a white solid which is soluble in water and can be obtained if the liquid left in the bottle is evaporated. It will be noticed that the element zinc has taken the place of the hydrogen in the sulfuric acid, liberating the hydrogen as the free element. This is a new kind of chemical change; it is known as **displacement.** Here *an element displaces one of the elements from a compound, setting it free, and unites with the rest of the constituents of the compound.*

Other metals beside zinc, such as magnesium, aluminum, and iron, may be used to displace the hydrogen of dilute sulfuric acid. Other acids, such as dilute hydrochloric acid, may be used instead of sulfuric.

38. Purification of hydrogen. When iron is used to prepare hydrogen, the gas has a distinct odor, due to the impurities usually present in iron wire or filings. Even when commercial zinc and acid are used, the impurities carried along give it a disagreeable odor. We may remove most of the impurities by passing the gas through a suitable solution containing sodium hydroxide and potassium permanganate; and then we may

absorb the water vapor by the use of a drying agent, such as granular calcium chloride. Hydrogen when pure is a gas without color, taste, or odor.

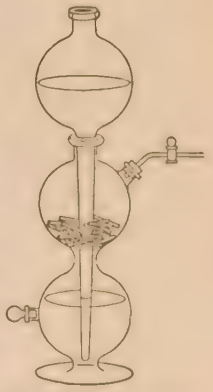


Fig. 26. Kipp generator.

39. Experiments with hydrogen. A steady stream of hydrogen can be conveniently produced by a Kipp generator. This apparatus (Fig. 26) is so arranged that it contains a small reserve of hydrogen in the middle bulb. When this reserve is drawn on by opening the stopcock, fresh acid automatically rises and acts on the zinc, which is also in the middle bulb; this action replenishes the supply of gas. If too much gas is generated, the acid is forced away from the zinc and the action stops. In this way a steady stream of gas is delivered.

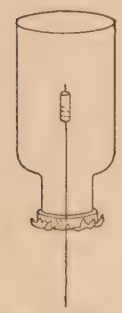


Fig. 27. Hydrogen burns, but the taper does not burn in it.

First we shall take a wide-mouthed bottle filled with hydrogen and apply a flame to its mouth: if the hydrogen is mixed with air, a slight pop results; but if free from air, it burns quietly.

If we lift up another bottle of hydrogen and hold it mouth down while we insert a lighted taper (Fig. 27), we find that the hydrogen burns around the mouth of the bottle and the taper is extinguished. On being withdrawn the taper is again lighted in passing through the burning hydrogen. The operation may be repeated several times until the hydrogen is burned up. This striking experiment shows *that hydrogen does not "support combustion."*

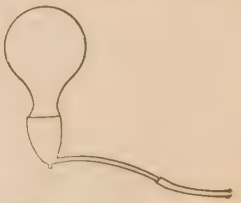


Fig. 28. Soap bubble filled with hydrogen.

To show how very light hydrogen is, we may attach a common clay pipe to a hydrogen generator and dip the bowl in a soap solution. We may thus fill soap bubbles with the gas (Fig. 28). When disengaged from the pipe each bubble rises rapidly in the air.

Another striking experiment which illustrates this same point is as follows: suspend an inverted beaker from one arm of a balance and then *pour hydrogen up into it* (Fig. 29). The beaker rises.

We shall next mix equal volumes of air and hydrogen by bringing a bottle when only half full of hydrogen up out of the pneumatic trough so that air takes the place of the water. When a flame is brought near such a mixture of gases, there is a loud explosion.

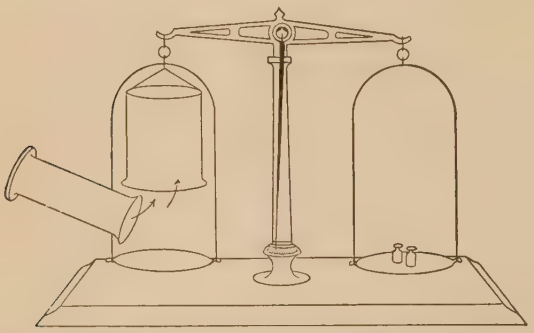


Fig. 29. Pouring hydrogen up into an inverted beaker.

When we have hydrogen unmixed with air, we may attach to the generator a clay-pipe stem to serve as a jet and may light the hydrogen. The flame is very hot but gives very little light; it is almost without color, being only slightly bluish.

In order to study the product of burning hydrogen in air, we attach a drying tube (*D* in Fig. 30) filled with calcium chloride between the jet and the generator. When all the air has been expelled from the apparatus, the hydrogen burns with a small flame. If we hold a cold, dry bell jar (*G*) over the flame (*F*), as shown in figure 30, water vapor is soon seen condensing on the jar, and after a short time drops of water (*W*) run down the sides.

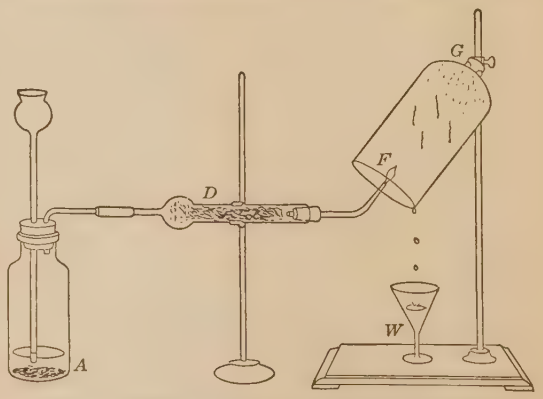


Fig. 30. Water is formed by burning hydrogen.

40. Properties of hydrogen. Such experiments show some of the characteristics of hydrogen. Like oxygen, it is a colorless, odorless gas when pure. It is sixteen times lighter than oxygen, being in fact the lightest

of all known substances. Since hydrogen is so light a gas, it escapes through small apertures most rapidly. This is the reason why a small rubber balloon filled with hydrogen collapses more rapidly than a similar balloon filled with illuminating gas. The solubility of hydrogen in water is very slight, being even less than that of oxygen.

Hydrogen can be liquefied by compression provided it is first cooled below its critical temperature * (− 234° C.). Liquid hydrogen is also colorless, and when allowed to evaporate rapidly, it freezes to a colorless solid.

41. Chemical behavior of hydrogen. We have seen that hydrogen burns in the air, and the product is the familiar compound of hydrogen and oxygen — water:

hydrogen + oxygen ⟶ water

Although hydrogen is itself readily combustible, yet *it is not a supporter of combustion;* that is, substances will not burn in it. At ordinary temperatures hydrogen is not an active element. But under certain conditions it does combine with many of the elements. For example, if a mixture of hydrogen and chlorine is exposed to the sunlight, the two gases will combine with explosive violence to form *hydrogen chloride.* Under the right conditions hydrogen combines with nitrogen to form *ammonia,* and with sulfur to form *hydrogen sulfide,* which is the gas that is characteristic of rotten eggs. If a mixture of hydrogen and oxygen is heated to about 800° C., a violent explosion occurs and water is formed.

We may prepare a mixture consisting of two volumes of hydrogen and one volume of oxygen (§ 11) and pass it into soapy water so that a froth of bubbles filled with the mixture is formed. *We first remove the generator* and then set the froth on fire with a long gas-lighting taper. The mixture explodes with a report like the shot of a gun.

* The critical temperature of a gas is the temperature below which it must be cooled before it can be liquefied by any pressure however great.

Although at a comparatively high temperature the combination of hydrogen and oxygen takes place with great violence, yet these two gases can be left together at room temperature for a very long time without chemical action. If, however, we introduce certain metals, such as finely divided platinum, chemical reaction sets in, and sometimes the platinum becomes so warm that it glows from the heat produced by the combination. The platinum undergoes no change, it merely acts as a **catalyst.** We may think of the catalyst as acting like oil which is applied to a machine as a lubricant. We grease the bearings to make the wheels go around more easily; we add a catalyst to make a chemical change take place at a lower temperature.

42. Reducing action. Hydrogen will not only combine with gaseous oxygen when heated, but will remove oxygen from many compounds.

Copper oxide is a black solid consisting of the two elements copper and oxygen. It may be formed by heating metallic copper in the air. This oxidation proceeds slowly and gradually converts all the elementary copper into the oxide.

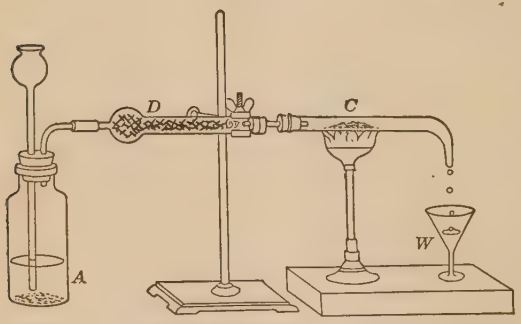


Fig. 31. Dry hydrogen is passed over hot copper oxide.

The apparatus shown in figure 31 is so arranged that dry hydrogen may be passed over hot copper oxide (*C*). The oxide is placed in the glass tube and heated with a burner until it is almost red-hot. Hydrogen is then passed over it. Water is formed and condenses in the tube. Metallic copper is left in the tube and can be recognized by its reddish color and metallic luster.

When hydrogen combines with the oxygen of a compound and thus removes it, we say the substance has been **reduced.**

Reduction is therefore essentially the removal of oxygen. During this process the hydrogen has combined with the oxygen, forming water. This change can be expressed thus:

$$\underset{[\text{copper}\ \text{oxygen}]}{\text{copper oxide}} + \text{hydrogen} \longrightarrow \underset{[\text{hydrogen}\ \text{oxygen}]}{\text{water}} + \text{copper}$$

The combining of a substance with oxygen we have previously defined as **oxidation.** Therefore the hydrogen has been oxidized, the copper oxide has been reduced. ***Reduction** is always accompanied by **oxidation.*** If one substance is reduced, some other substance must be oxidized. Besides hydrogen there are other substances, such as carbon, which act as reducing agents, and we shall later see that the terms "oxidation" and "reduction" are often given a somewhat wider meaning.

43. Uses of hydrogen. Hydrogen gas has a few practical applications. Because it is the lightest known gas it has long been used to fill balloons and dirigible airships; but on account of the danger of explosions it has recently been replaced in the United States by helium. This new gas is somewhat heavier than hydrogen, but it is not combustible. It also enters into the process by which certain vegetable and animal oils are changed into hard fats. This process is called **hydrogenation** and will be described in Chapter XXX.

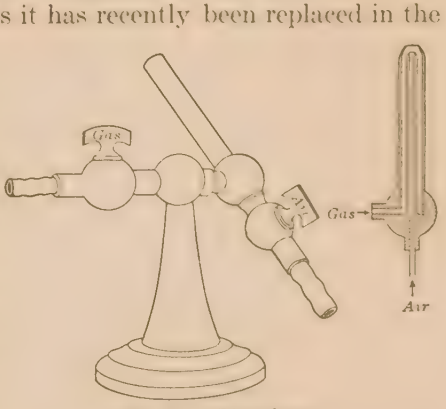


Fig. 32. Blast lamp.

The flame of burning hydrogen is intensely hot and is particularly so if oxygen is forced into it in a suitable burner. This burner is very similar to that shown in figure 32, which is an ordinary **blast lamp**

using illuminating gas and air instead of hydrogen and oxygen. The oxyhydrogen flame is used when a very intense heat is desired, such as in melting platinum and other metals with high melting points. It is also used in "lead burning," which is the process of melting and joining sheet lead or lead pipe together to make one piece. A very recent application for hydrogen is in the so-called "atomic hydrogen" flame shown in the frontispiece, which will be explained further in Chapter VIII. Hydrogen is also used in the manufacture of synthetic ammonia, which will be described in Chapter XX. Some hydrogen has also been used to manufacture hydrochloric acid on a commercial scale by combining hydrogen with chlorine. Large quantities of hydrogen mixed with carbon monoxide are used as fuel under the name of water-gas. Hydrogen for commercial purposes is usually prepared by the electrolysis of water. This process was explained in Chapter II. It is also prepared as a by-product in the manufacture of chlorine by the electrolysis of brine (Chapter XII).

44. Diffusion. When a cylinder of hydrogen is placed mouth downwards over another cylinder containing oxygen and allowed to stand a few minutes, we find that the cylinders contain a homogeneous mixture of gases. This means that the hydrogen gas in spite of its lightness has moved downwards and the oxygen, which is nearly 16 times as heavy as hydrogen, has moved upwards. The material of all gases has this extraordinary power of motion. This process by which the particles of substances tend to become uniformly intermingled is called **diffusion.** The rates at which different gases diffuse into a particular gas, such as air, are approximately inversely proportional to the square roots of their densities. This means that hydrogen would mix with air 4 times as rapidly as oxygen. In fact, hydrogen has the greatest speed of diffusion of all gases.

We may show the diffusion of bromine vapor, which is about 5 times as heavy as air, by pouring a little liquid bromine into a cylinder. The red liquid quickly evaporates and diffuses up through the whole cylinder (Fig. 33).

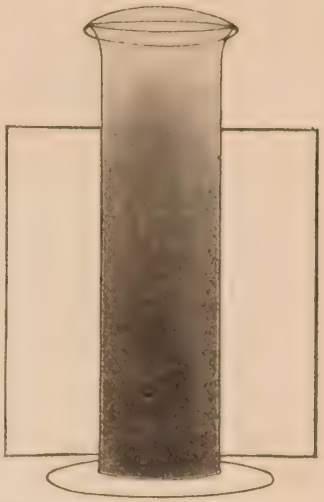


Fig. 33. Diffusion of bromine vapor upward.

45. The kinetic-molecular theory. To explain the diffusibility of gases and also the general behavior of gases as expressed in the gas laws of Boyle and Charles (See Appendix), a theory has been made which is known as the **kinetic-molecular theory.** It is now generally supposed that all gases are made up of exceedingly minute particles called **molecules.** We think that all the molecules of a given substance are alike. In solids and liquids these molecules are fairly close together, but in gases they are widely scattered with much vacant space between them.

Then, too, it is assumed that these little particles are flying about in all directions with great speed and traveling in straight lines, except when they hit each other and bounce off. The molecules of a gas seem to have no inherent tendency to stay in one place. This explains why gases diffuse so quickly and fill the whole interior of a containing vessel. Because the molecules of all substances under ordinary conditions are supposed to be in rapid motion, they must possess **kinetic energy.**

The blows which these molecules of a gas strike against the surrounding walls constitute a continuous force tending to push out these walls. This accounts for gas pressures. According to this theory the expansion of a gas when heated is due to the more rapid movement of its molecules and to

their requiring, in consequence, more room in which to fly about. All laws of gases can be explained by this **kinetic-molecular theory.**

SUMMARY OF CHAPTER IV

HYDROGEN MAY BE PREPARED by:

(*a*) reaction between water and a metal;

(*b*) displacement in an acid by a metal (usual laboratory method);

(*c*) electrolysis of water (commercial method).

HYDROGEN is a *colorless*, *odorless* gas. It is the lightest known gas and diffuses more rapidly than any other gas.

HYDROGEN BURNS in oxygen or air, forming water. It is a powerful *reducing* agent. When a substance is reduced by hydrogen, the hydrogen in turn is *oxidized*. Reduction is always accompanied by oxidation.

USES OF HYDROGEN: For filling balloons and dirigibles, for the hydrogenation of oils, for the oxyhydrogen flame used to produce intense heat, for the preparation of synthetic ammonia, and (mixed with other gases) as a fuel.

THE KINETIC–MOLECULAR THEORY of gases assumes (1) that a gas is a vacant space with exceedingly minute particles scattered throughout, and (2) that these particles (molecules) under ordinary conditions are flying about in all directions with great speed.

Questions

1. In what properties are hydrogen and oxygen alike? In what are they unlike?

2. What property has hydrogen which makes it a dangerous substance with which to inflate balloons?

3. How would you test hydrogen to see if it were contaminated with air?

4. How would you arrange a bottle of hydrogen to keep it overnight?

5. Could pure hydrogen be used in a Bunsen burner instead of illuminating gas?

6. What is the essential difference between oxides and hydroxides?

7. In the experiment of burning hydrogen to form water, why is it necessary to dry the hydrogen?

8. Why is oxygen passed through the inner tube of the oxyhydrogen blowpipe rather than the outer?

9. Do we ever have oxidation without reduction?

10. Name the three types of chemical reactions which have been studied thus far and describe briefly an example of each.

11. Is it necessary to use a pneumatic trough in collecting hydrogen?

12. Explain how the thistle tube in the hydrogen generator acts as a safety tube.

13. Hydrogen can be ignited by holding finely divided platinum in a jet of the gas. Explain.

14. Would pure hydrogen furnish a satisfactory illuminating gas? Explain.

15. All the air must be swept out of the hydrogen generator before the gas is ignited at the delivery tube. How would you test your apparatus?

CHAPTER V

WATER AND ITS COMPOSITION. HYDROGEN PEROXIDE

Occurrence and importance — characteristic properties — change of state — solvent power of water — impurities in water — purification of drinking water.

Chemical composition of water — electrolysis — synthesis by volume — Gay-Lussac's Law of Volumes — synthesis by weight — percentage composition.

Hydrogen peroxide — composition, properties, and uses.

46. Occurrence and importance. Water is the most familiar of all chemical compounds. It covers about five-sevenths of the earth's surface and is present in varying amounts in many of the commonest objects. The soil under normal conditions contains water, which, as we all know, is necessary to the growth of plants. The plants themselves contain large quantities of it; in fact, most of the vegetables used for food are at least three-quarters water. Milk is about 87 per cent water, and certain vegetables, such as cucumbers and tomatoes, contain as much as 95 per cent water. The human body consists of about 70 per cent water, which is derived from our food and drink. The presence of water vapor in the atmosphere, its formation into rain and snow under varying conditions, and the important part it plays in climatic changes are familiar to everyone. Because water is fundamentally so important in the growth of plants and animals and in the production of climatic changes, it is not too much to say that life without it is impossible.

47. Characteristic properties. Pure water is an odorless liquid. In small quantities it is colorless, but large masses show a distinctly blue color. When sufficiently cooled, it solidifies to a

colorless solid commonly known as ice; when heated it boils and changes rapidly into water vapor, or, as it is usually called, steam.

One cubic centimeter of water at 4° C. weighs 1 gram. Its **density** at 4° is, therefore, one gram per cubic centimeter. The **specific gravity** of a substance is the ratio of its density to the density of water. Thus, the specific gravity of mercury is 13.6, which means that it is 13.6 times as heavy as water.

48. Changes of state. When liquid water freezes into ice or boils off as steam, we say that it has changed its state. All materials can be classified as **solid, liquid,** or **gaseous.** These are called the three states of matter. The transformation from one to another is a purely physical change, and the temperature at which it takes place is a very important physical property of the substance. The temperature at which water freezes to ice is taken as 0° on the centigrade thermometer and is marked 32° on the Fahrenheit scale. The centigrade scale is the one that is used in nearly all scientific work. The temperature at which solid ice melts to water is also 0° C. Liquid water is always passing to some extent into the gaseous state, a process which is called **evaporation,** familiar to everyone as the way in which wet clothes slowly dry. Since water vapor is a gas, it is invisible, and the white clouds which are sometimes called steam are not gaseous water at all, but consist of very fine drops of water formed by the vapor as it suddenly returns to the liquid condition.

We may demonstrate that gaseous water, or "live steam," is invisible by the following experiment. We place a little water in a large flask provided with a one-hole stopper and bent tube, as shown in figure 34. When the water boils rapidly, a cloud of "steam" escapes from the tube. It will be seen that the flask is clear al-

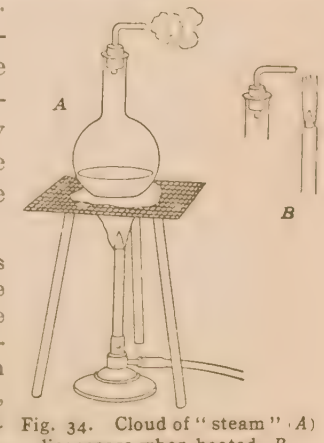


Fig. 34. Cloud of "steam" (*A*) disappears when heated (*B*).

though full of steam. If we now hold under the jet of steam another Bunsen burner (Fig. 34 *B*), the cloud at once disappears because the flame has warmed the air so that the steam does not condense.

The evaporation of water at ordinary temperatures is slow but becomes more rapid as the temperature rises. When the temperature is raised sufficiently high, bubbles of water vapor rise through the liquid and the water is said to **boil.** At this point the evaporation is very rapid. The temperature at which this phenomenon takes place depends on the barometric pressure (Appendix). The boiling point of water at 760 mm. pressure is 100° C. The temperatures at which a substance melts and boils are called the **melting point** and the **boiling point** respectively.

49. Solvent power of water. Water will dissolve a great many substances; for example, salt and sugar. This process, in the simpler cases at least, is probably merely a mechanical one. We may consider the liquid which is formed by dissolving sugar in water (called a **solution**) as a mixture. We use water to make solutions of a great many different substances, both because water is cheap and easily obtained and because it will dissolve so many materials. We speak of the liquid which is used in making a solution as the **solvent;** we express the ease with which water dissolves substances by saying it has great solvent powers. (See Table of Solubilities in Appendix.) A water solution of a material is often called an **aqueous solution.**

50. Natural water is impure. Since water is such an excellent solvent it is never found pure. Sea water, for example, has a considerable amount of common salt and many other substances dissolved in it. Water obtained from certain wells and springs contains only a small amount of dissolved material; but the purest form of natural water is rain water. Even this, however, contains dust from the air and dissolved gases. Besides the dissolved impurities, natural water usually has a great deal of material mechanically suspended in it. This generally

consists of very fine particles of soil and causes what is commonly called " muddy water."

Still another sort of impurity is organic matter, which is partially suspended and partially dissolved and which consists of compounds formed from plants and animals. These come from the plant life in the soil and from sewage. Associated with the organic material and living on it are microörganisms, or bacteria, many of which cause disease. Their presence in water is almost always due to contamination with the waste products of animal life. Certain diseases — for example, typhoid fever — are often contracted by drinking water which is thus polluted and into which the typhoid bacteria have found their way from persons suffering with the disease. Because water contaminated with sewage is very dangerous, towns and cities must go to extreme measures to obtain their supply from uncontaminated sources, and, if this is impossible, to purify carefully the water which is used.

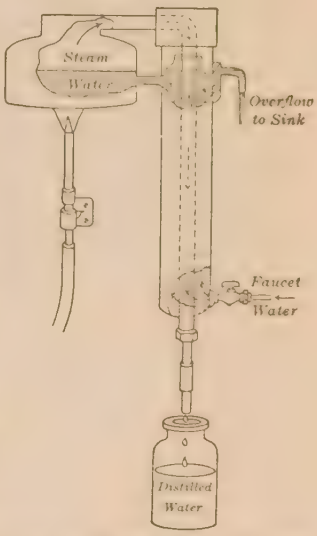


Fig. 35. Making distilled water in the laboratory.

51. Purification of water. *Water may be purified in four ways.* Only the first produces really pure water. The other methods remove or destroy some of the materials which make it unfit for drinking purposes.

(1) ***Distillation.*** All the dissolved and suspended materials can be removed by a process called **distillation.** The water is boiled in a vessel which is so arranged that the steam will pass through a cold tube and again return to the liquid condition (Fig. 35). This change of water vapor to liquid water is called condensation, and the apparatus in which it takes place is

called a **condenser.** The water which drops from the end of the condenser is pure, the impurities being left behind in the vessel in which the water was boiled. **Distilled water,** as it is called, is used in the laboratory when pure water is desired. It is sometimes used for drinking purposes but has a peculiar "flat" taste because it contains no dissolved air or other materials.

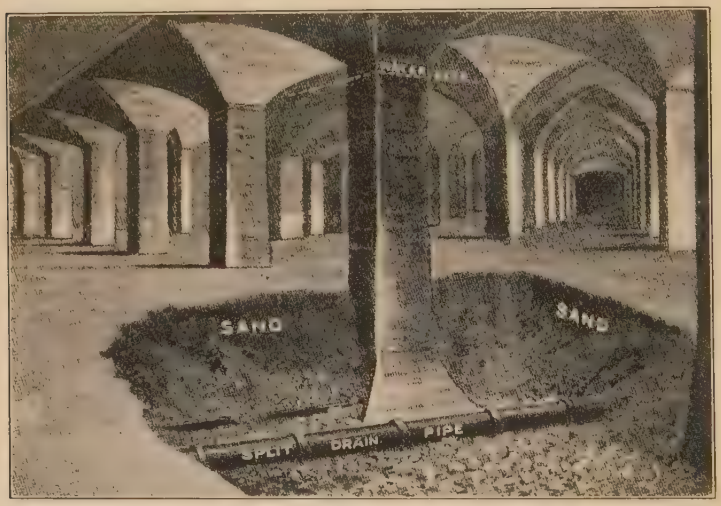


Fig. 36. Beds of sand for filtering water.

This taste may be partially removed by bubbling air through the water, which dissolves a small quantity of the air and thus becomes more palatable.

(2) ***Filtration.*** The suspended material in water may be removed by filtration. This is done on a large scale in cities where the only supply comes from muddy rivers, or similar sources. The water is allowed to pass slowly through beds of gravel and sand (Fig. 36). The suspended material is caught between the small particles of the sand and retained. The water issuing from the bottom of the filter bed still contains all the *dissolved* impurities, but it is free from suspended matter.

(3) ***Boiling.*** Water which contains harmful bacteria may be made fit to drink by boiling for a short while. This so-called process of purification does not really remove any of the impurities, but merely kills the microörganisms (Fig. 37) which cause disease. These minute forms of plant life cannot live at the temperature of boiling water. When they are dead they can no longer cause disease. This method of treating water is very effective from the standpoint of health, but is too expensive to be utilized except on a small scale in special emergencies.

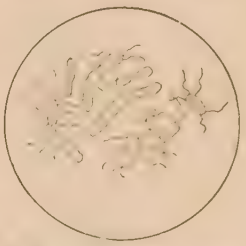


Fig. 37. Bacteria sometimes found in drinking water. (Greatly magnified.)

(4) ***Chemical treatment of drinking water.*** The bacteria may be destroyed by other methods besides boiling. A number of chemical substances when added to water in very small amounts kill the microörganisms. Chlorine and hypochlorous acid are two such materials; but we shall reserve a full discussion of this method of purification until we have considered these substances. This process of chemical purification is rapidly becoming very important. A process closely akin to it is the way in which natural running water will in time purify itself. The oxygen of the atmosphere dissolves in the water and chemically acts on the bacteria, destroying them. This is a slow process, but in a modified form has been used to some extent for purifying city water. The water is sprayed into the air in fountains, thus allowing as much opportunity as possible for the chemical action of the air.

Composition of Water

52. Decomposition of water. We have already seen (§ 11) that water may be decomposed by an electric current into hydrogen and oxygen. This chemical change can be represented thus:

$$\text{water} \longrightarrow \text{hydrogen} + \text{oxygen}$$

Besides this fact we recall that the volume of hydrogen generated was double that of the oxygen. Knowing the densities of hydrogen and oxygen we might compute the *weights* of these gases, which are the constituent elements in water, and so get the percentage composition of water.

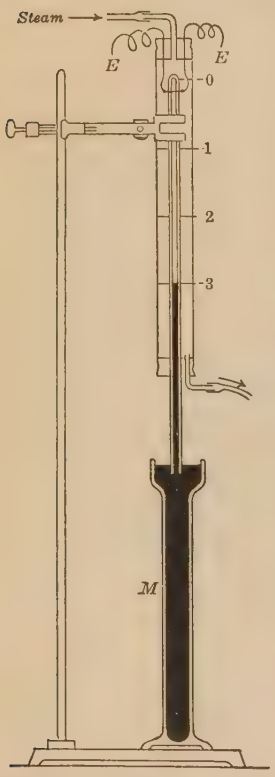


Fig. 38. Volume of steam produced by union of hydrogen and oxygen.

53. Synthesis of water by volume. The electrolysis of water is a method of decomposition, or **analysis,** which means "tearing apart." A more decisive determination of the composition of water is brought about by an actual observation of the fact that the gases hydrogen and oxygen unite in the proportion of two volumes of hydrogen to one of oxygen to form water. This process of experimentation is called **synthesis,** which means "putting together."

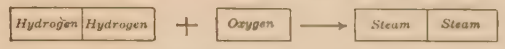
The experiment of combining the two gases is usually carried on in a piece of apparatus called a **eudiometer.** This is a graduated glass tube with two platinum wires fused through the glass near the closed end. There is a spark gap of 2 or 3 mm. between the ends of the wires. The tube is first entirely filled with mercury and inverted in a jar of the same liquid. Then a mixture of one volume of oxygen and two volumes of hydrogen is prepared by electrolysis and introduced into the tube until it is about three-fourths full of gas. An electric spark from an induction coil causes the gases to combine, and at once we see that the mercury rises until it reaches the top of the tube. The water formed has condensed to a slight dew.

If the experiment is performed with the tube surrounded by a wider one through which steam passes (Fig. 38), the condensation of the

resulting steam is prevented. In this case it is found that, when all the gases are measured at the same temperature (about 100° C.) and at the same pressure, *a shrinkage of one-third has occurred.* (Care must be taken to adjust the apparatus so that the top of the mercury in the tube, both before and after the change, is at the same height above the free surface of the mercury in the jar.)

This experiment shows that the volume of the steam is just equal to the volume of the hydrogen. In other words,

2 vol. hydrogen + 1 vol. oxygen ⟶ 2 vol. steam.



54. Gay-Lussac's law of volumes. It is astonishing that the combining volumes of these gases should bear this simple and exact ratio to one another. When other gases are carefully studied in the same way, it is found that the ***volumes of gases*** *used and produced in a chemical change can always be represented by the ratio of* ***small whole numbers.*** This exceedingly interesting fact was discovered by Gay-Lussac (Fig. 39) in 1808.

Fig. 39. Joseph Louis Gay-Lussac (1778–1850). A French chemist famous for his researches on combining volumes of gases.

55. Composition of water by weight. To determine the relative *weights* of the elements which are combined in water, we take advantage of the reaction between hydrogen and copper oxide. In this experiment we weigh the water produced by reducing a known weight of copper oxide. The

loss in weight of the copper oxide gives us the weight of the oxygen used, and the difference between the weight of the water formed and the weight of the oxygen gives the weight of the hydrogen. The apparatus is essentially the same as that already shown in figure 31. The copper oxide (*A* in Fig. 40) is reduced; the water is collected and weighed in a U-tube (*B*) containing a drying agent, such as calcium chloride.

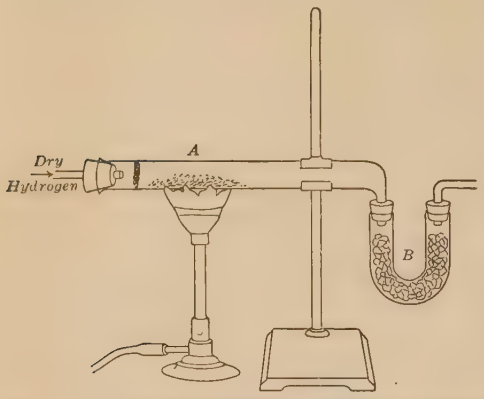


Fig. 40. Apparatus for finding the relative weights of hydrogen and oxygen in water.

This method of determining the composition of water was first used in 1820 by Berzelius, and the work was repeated in 1843 by Dumas. In more recent years the American chemist Morley (Fig. 41) has determined the composition of water with very great precision. According to the results of his experiments, ***1 part** by weight of hydrogen combines with **7.94** parts by weight of oxygen to form water.* This is often called the **gravimetric synthesis** of water.

Such an experiment, in which the weights or volumes of the materials involved are carefully measured, is called a **quantitative** experiment. The other sort of experiment, in which we observe only the nature of the change and the properties of the products, is called a **qualitative** experiment.

56. Percentage composition of water. This experiment illustrates very well the Law of Definite Composition; for it is found that all samples of pure water, from whatever source, show when analyzed that 1 part by weight of hydrogen has

combined with 7.94 parts by weight of oxygen. From the fact that there is no change in weight during a chemical change (Law of Conservation of Matter), we know that the hydrogen must be $\frac{1}{1+7.94}$ or 11.2 per cent of water, and that the oxygen must be $\frac{7.94}{1+7.94}$ or 88.8 per cent of water. In other words, *water is about $\frac{8}{9}$ oxygen and $\frac{1}{9}$ hydrogen by weight.*

Fig. 41. Edward Williams Morley (1838-1923). An American professor of chemistry who determined with great precision the composition of water.

Hydrogen Peroxide

57. Composition. There is a second compound of hydrogen and oxygen which contains twice as much oxygen combined with the same weight of hydrogen as does water. We have just seen that water is composed of 1 part of hydrogen and 7.94 parts of oxygen by weight; but hydrogen peroxide is composed of 1 part of hydrogen and 2×7.94 or 15.88 parts of oxygen by weight. The prefix *per* means that this compound contains more oxygen than the usual hydrogen oxide (water).

58. Preparation and properties. Industrially hydrogen peroxide is made by the action of *cold dilute* sulfuric acid on barium peroxide, a white powder which is an oxide of barium, a metal much like calcium. This action may be expressed as follows:

barium peroxide + sulfuric acid ⟶ barium sulfate + hydrogen peroxide

[barium, oxygen] [hydrogen, sulfur, oxygen] [barium, sulfur, oxygen] [hydrogen, oxygen]

The barium sulfate is a white, insoluble solid, which can be removed by filtration.

Hydrogen peroxide can be prepared as an absolutely pure substance, but it is extremely unstable and is never used except in dilute solutions. It is commonly sold as a 3 per cent solution in water under the name of **hydrogen peroxide.** Since it slowly gives off oxygen, bottles containing the solution often have their corks wired in. The commercial hydrogen peroxide solution yields 10 times its volume of oxygen and so is sometimes called a " 10-volume solution."

59. Uses. Like ozone its readiness to give up oxygen makes hydrogen peroxide a strong *oxidizing agent.* This is the reason for its use in bleaching silk, wool, hair, feathers, and ivory. It is also used in medicine as an antiseptic and cleansing agent. The action of hydrogen peroxide as a germicide has been overestimated. Because of its property of giving off free oxygen when in contact with open wounds and because of the mechanical action of this evolved gas, it does serve to cleanse the wound and to remove any foreign material. It is especially valuable for expelling pus and for loosening dried bloody bandages.

SUMMARY OF CHAPTER V

WATER is one of the most *important compounds.*

Water exists in *three states:* solid (ice), liquid, and gaseous (steam). It freezes at 0° C. and boils at 100° C. One cubic centimeter of water at 4° C. weighs 1 gram.

Water is an excellent *solvent* for many substances; resulting solutions are called *aqueous solutions.*

NATURAL WATERS are impure; they contain dissolved and suspended material and sometimes bacteria.

PURE WATER can be prepared by *distillation.* Suspended material may be removed by *filtration.* Disease bacteria may be destroyed by boiling, or by adding small amounts of certain chemicals.

THE COMPOSITION of water can be shown by *analysis* and by *synthesis.* Two volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

LAW OF GAY–LUSSAC: The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.

COMPOSITION OF WATER BY WEIGHT: 1 part by weight of hydrogen and 7.94 parts by weight of oxygen.

HYDROGEN PEROXIDE is composed of 1 part by weight of hydrogen and 2×7.94 or 15.88 parts by weight of oxygen. It is a strong oxidizing agent and is used for bleaching and as an antiseptic.

Questions and Problems

1. How would you prove that a certain colorless liquid was water?
2. How would you proceed to determine the total amount of solids present in a sample of water?
3. Why is rain water the purest form of natural water?
4. How could a steamship in mid-ocean obtain a supply of drinking water?
5. Can water be purified by freezing?
6. How would you destroy bacteria in water?
7. How could you prove that the air of the laboratory contains water vapor?
8. How could you demonstrate that "live steam" is colorless?
9. Name two or more other substances besides water which exist in three states.
10. Name two other common solvents besides water.
11. Why do we need to drink water?
12. If one liter of hydrogen under standard conditions* weighs 0.09 grams, and one liter of oxygen under the same conditions weighs 1.43

* Standard conditions are 0° C. and 760 mm. See Appendix.

grams, calculate from the results of the electrolysis of water its composition by weight.

13. Calculate the weight of hydrogen which will unite with 500 cc. of oxygen and leave no free oxygen.

14. When 20 cc. of hydrogen and 8 cc. of oxygen are placed in a eudiometer and ignited, what volume of steam is formed? What gas and how much of it remains in excess?

15. When 20 cc. of hydrogen and 20 cc. of oxygen are mixed in a eudiometer and ignited, (*a*) what volume of steam is formed? (*b*) What gas and how much of it remains in excess?

16. In studying the composition of water by weight Dumas obtained the following results:

Weight of water formed	945.439 g.
Oxygen taken from copper oxide	840.161 g.
Weight of hydrogen in water	105.278 g.

Compute the percentage composition of water from these figures.

17. A current of steam is passed over some clean iron filings which weigh 4.131 g. The iron filings are found to have increased in weight to 4.846 g. (*a*) What weight of steam has been decomposed in this experiment? (*b*) What weight of hydrogen has been set free? (*c*) What volume would it occupy under standard conditions?

(Assume 1 liter of hydrogen weighs 0.09 grams.)

18. Morley found in one of his experiments that 3.2645 grams of hydrogen combined with 25.9176 grams of oxygen. Compute the ratio in which the hydrogen and oxygen unite.

19. Compare hydrogen peroxide and ozone by pointing out the resemblances and differences.

Topics for Further Study

Drinking water. What is the source of your water supply? What methods of purification are used? Make a trip to the local water works. Is the appearance of water a safe indication of its desirability for drinking purposes? (*Chemistry in Industry*, Vol. 2.)

Importance of water to life. What is the rôle of water in climatic changes? Is the prosperity of a country affected by the rainfall? What has been done in recent years to supply water to arid regions? How do you account for the presence of so much dissolved material in the sea, and so little in rivers, ponds, and most lakes? (*Science Remaking the World.*)

Review Questions

1. Write a careful statement of *three* fundamental laws which we have studied thus far.

2. Describe a laboratory experiment to illustrate each of these laws.

3. Write out a definition of each of the following terms as used in chemistry: (*a*) *element*; (*b*) *substance*; (*c*) *mixture*; (*d*) *compound*; (*e*) *catalyst*.

4. Describe a method for preparing hydrogen in quantity and make a sketch of the apparatus used.

5. Describe one experiment to determine the composition of water by *volume*, and another experiment to determine its composition by *weight*.

CHAPTER VI

THE TWO OXIDES OF CARBON

Dioxide — occurrence in air — production by burning and decay — test — used by plants — preparation by action of acids on carbonates — experiments — properties — liquid and solid — commercial uses.

Monoxide — produced in coal fire — by reduction — from formic acid — properties — uses.

Composition of the dioxide and monoxide — Law of Multiple Proportions.

Carbon Dioxide

60. Occurrence in the air. Carbon dioxide is always present in the atmosphere although never in large quantities. It varies from 4 parts in 10,000 parts of air in the country to about 1 per cent in crowded rooms. It also occurs in natural waters and in the soil. In certain volcanic localities it escapes from fissures in the earth's crust. For example, near Naples there is a cave in which the air at the bottom contains so large a proportion of carbon dioxide that a dog would be overcome ; and in the Yellowstone Park there is a valley where animals have died because suffocated in carbon dioxide. This gas collects in certain mines and so is called by the miners "choke damp." Since it is heavier than air, it often collects in the bottom of old wells, cisterns, and "clean-outs" for sewer pipes. It is not perceptible, and hence many people have lost their lives. This danger may be avoided by testing with a lighted lantern. If the flame is extinguished, there is insufficient oxygen for life.

61. Production of carbon dioxide. When we burned charcoal (carbon) in oxygen (§ 22), the product was a gas which

we called carbon dioxide. This process is going on all about us wherever charcoal, coke, coal, or wood — fuels which are largely composed of carbon — are being burned. This same gas is being produced on an even greater scale by the slow combustion of food in animals, and by the decay of wood and dead leaves.

One of the essentials of the life process in animals is the slow oxidation of the food which has been consumed; this oxidation liberates the heat which keeps the body warm. The oxidation takes place by means of the oxygen of the air which is breathed. The products of the combustion — carbon dioxide and water vapor — are exhaled with each breath.

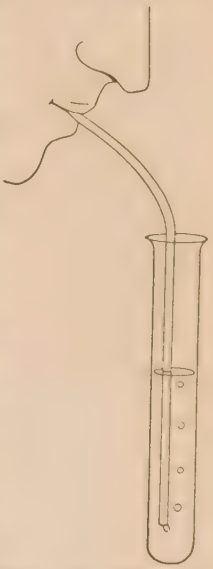


Fig. 42. Blowing through limewater to show the presence of carbon dioxide in the breath.

62. Tests for carbon dioxide. We may prove that carbon dioxide is present in the breath by a simple experiment. If by means of a glass tube we blow through some clear limewater * in a large test tube, as shown in figure 42, we notice that at first the breath bubbles produce practically no change; but as soon as the breath comes from farther within the lungs, the clear liquid quickly becomes milky, showing the presence of carbon dioxide. *The production of milkiness in limewater is a characteristic of carbon dioxide.*

To demonstrate the fact that carbon dioxide is produced when any carbon compound is burned in the air, we may set fire to a piece of paper and drop it while burning into a dry bottle. We then pour in a little limewater, cover the bottle with a glass plate, and shake it up.

We may also hold a dry bottle inverted over a candle flame and show the presence of carbon dioxide by means of limewater.

* To make limewater, place a handful of powdered lime in a big bottle and fill this up with water; cork it up and shake it for a minute. Then leave the mixture overnight to settle and pour off the clear solution for use.

63. How plants use carbon dioxide. At first thought it would seem that the constant production of this great amount of carbon dioxide must fill the atmosphere with the gas. The fact is, however, that when pure air in the country is analyzed, it is never found to contain more than three or four hundredths of one per cent of it. This is because most plants reverse the process which takes place in animals; they absorb carbon dioxide from the air and give off oxygen.

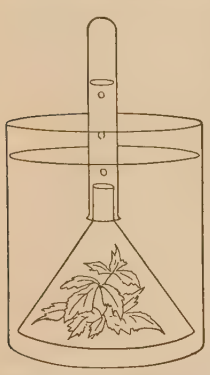


Fig. 43. Green leaves give off oxygen.

The liberation of the oxygen can easily be shown by placing fresh green leaves under water (saturated with carbon dioxide) in a jar, as in figure 43, and then setting the jar in the sunlight. Bubbles of gas appear on the leaves, grow larger, and then detach themselves and rise to the top. This gas may be collected in a test tube and tested with a glowing splinter of wood. *It is oxygen.*

We shall see in the next chapter that the small amount of carbon dioxide in the air varies very little; it is of the greatest significance because of the intimate relation it bears to the life of all plants and animals.

64. Preparation of pure carbon dioxide. It is possible to prepare pure carbon dioxide by burning carbon in oxygen, but it is difficult to separate the gas from the unused oxygen. In the laboratory it is usually prepared by the action of an acid on marble, which is a chemical compound called calcium carbonate made up of the elements calcium, carbon, and oxygen. When a dilute acid, such as hydrochloric acid, is brought into contact with a carbonate, a vigorous **effervescence,** or bubbling, takes place and continues until either the marble or the acid is all used up. This effervescence somewhat resembles boiling, except that the vapor which rises in **boiling** is always the same substance as the liquid from which it comes.

To collect the gas evolved in this chemical action we may use the same apparatus as in preparing hydrogen (Fig. 25). Pieces of marble

are placed in the bottle, and dilute hydrochloric acid is poured in through the thistle tube. The action starts at once, and the gas may be collected as usual in bottles in the pneumatic trough.

65. Experiments with carbon dioxide. To study the properties of this gas we may perform the following experiments:

(1) A lighted taper is inserted into a bottle of the gas. The flame is at once put out. *What property does this show?*

(2) We dip a stirring rod into some limewater and then withdraw it so that a clear drop hangs from its end. If this is lowered into a bottle of the gas, it immediately becomes clouded, or milky, in appearance. *This is a* ***test*** *for carbon dioxide.*

(3) We may lower a short piece of lighted candle into a wide-mouthed beaker and then pour the gas from one of the bottles over the candle. The candle goes out. *What does this show about the relative densities of this gas and air?*

(4) Let us color some water with a few drops of a dye solution known as litmus, and let gas from the generator bubble through it for a few minutes. It will be noticed very soon that the *litmus has turned* ***red****, which is a proof of the presence of an* ***acid****.* This gas dissolves to a small extent in water, and the resulting solution, as we have seen, is an acid. For this reason the gas is often called in commerce "carbonic acid gas."

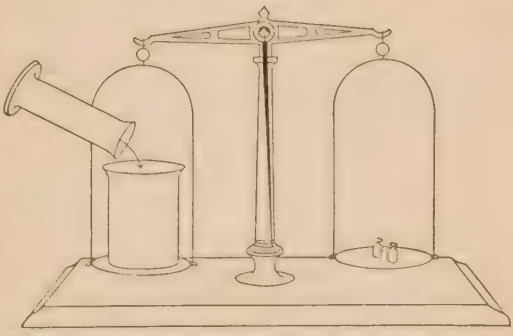


Fig. 44. Scale pan weighed down by carbon dioxide.

66. Properties of carbon dioxide. In our experimental study we find that carbon dioxide is a gas without color or odor. Since it is a little more than one and one-half times as heavy as air, it can be poured from one vessel into another almost like water (Fig. 44). It is somewhat soluble in water. As with all gases, its solubility is greatly increased by increase in pressure and, conversely, becomes less with diminished pressure. This fact is taken advantage of in

so-called **carbonated water,** and in many beverages, such as ginger ale. The beverage is treated with carbon dioxide under pressure and dissolves considerable quantities of the gas. The bottle containing the liquid is closed while still under pressure. When the cork is removed the gas escapes and produces the familar effervescence (Fig. 45).

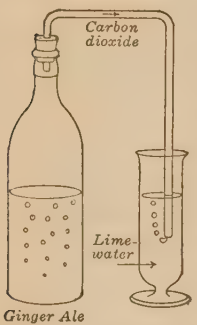


Fig 45. Carbon dioxide evolved from ginger ale causes a precipitate in limewater.

The most characteristic chemical property of carbon dioxide is its inertness. It will neither burn nor support combustion. It readily combines with one class of substances called **alkalies,** forming a group of compounds named the carbonates. Lime is an alkali which is chemically known as calcium hydroxide, and the white precipitate which is formed when limewater and carbon dioxide react is calcium carbonate. This calcium carbonate is exactly the same chemical compound as ordinary marble, and is called " precipitated chalk."

67. Liquid and solid carbon dioxide. By applying sufficient pressure to carbon dioxide gas at ordinary temperatures it may be condensed to a liquid. This liquid is an article of commerce and is put on the market in strong steel tanks. When the liquid carbon dioxide runs from such a tank, part of it evaporates quickly and removes so much heat that the rest is frozen to a snow-like solid.

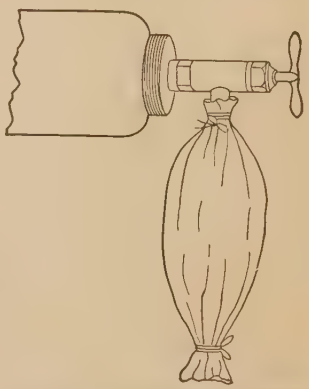


Fig. 46. Liquid carbon dioxide boiling and freezing.

A tank of carbon dioxide is tilted on its side, as shown in figure 46. A stout flannel bag is tied around the outlet, and the valve is opened wide. After a few minutes the bag is found to contain a snow-like solid. This solid has very fascinating properties. It quickly disappears when

left by itself, as it rapidly changes into gas. A portion of it placed on water very soon evaporates, but in so doing it removes heat from the water and freezes the latter.

If the solid is put in a beaker and mixed with ether, the mixture will freeze a test tube of mercury. The ether serves to carry the heat quickly from the test tube to the solid.

CAUTION. In handling the solid carbon dioxide one must avoid pressing it against the flesh, otherwise it causes a frost bite which feels very much like a burn.

Solid carbon dioxide enables us easily to reach a temperature as low as $-78°$ C. It is sometimes used for refrigeration purposes.

68. Commercial uses. Carbon dioxide has a number of important uses. We have already mentioned its extensive use in the preparation of carbonated beverages. The **soda water** of the drug store, which was originally prepared by mixing baking soda in solution with some fruit acid, is now made by connecting a tank of the gas with a supply of water in such a way that a solution of carbon dioxide issues when the faucet is opened. One type of **fire extinguishers** (Fig. 47) depends on carbon dioxide for its effectiveness. The body of the container is filled with the water solution of a carbonate, generally sodium bicarbonate. A small bottle at the top contains sulfuric acid. When the extinguisher is turned upside down, the acid comes in contact with the carbonate and produces carbon dioxide. The gas thus produced forces the liquid out through the hose and also comes out itself. Since carbon dioxide is heavy and noninflammable, it partially excludes the oxygen of the air and assists the water in putting out the fire. Such extinguishers are very effective but somewhat heavy to handle. In many electrical power plants a battery of steel tanks containing liquid carbon

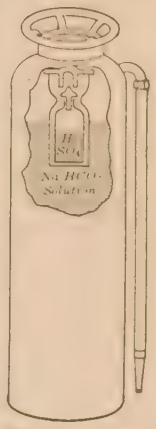


Fig. 47. Carbon dioxide fire extinguisher.

Fig. 48. Tanks of liquid carbon dioxide used to put out fires in electric power plants and on boats.

dioxide (Fig. 48) is arranged to liberate the gas in case of fire.

69. Carbon dioxide foam. One difficulty with the carbon dioxide extinguisher is that the gas diffuses rapidly. A new method has been devised by which the carbon dioxide gas is confined in tough, durable bubbles of foam or froth. These float on burning oil or adhere to a burning surface. This method, known as the **foamite** method, has proved especially effective in fighting oil fires (Fig. 49) and also fires in buildings that have not gained much headway. The carbon dioxide is generated by the action between solutions of sodium bicarbonate (baking soda) and aluminum sulfate (alum). The foamite is obtained by extraction from licorice root and is mixed with the sodium bicarbonate solution. Its purpose is to prevent

From *Wide World Photos.*

Fig. 49. A ten-million dollar oil fire in California. Oil tanks can now be protected by foamite.

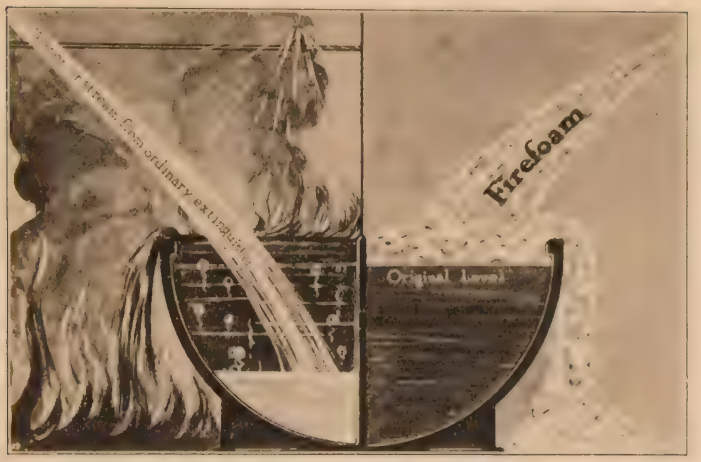


Fig. 50. Diagram to show the effect of water (left) and firefoam (right) on burning oil.

the escape of the gas. The result is that a blanket of foam several inches thick floats on the burning liquid and shuts off the supply of oxygen (Fig. 50).

Carbon Monoxide

70. Formation in a coal fire. When carbon or a substance containing carbon burns in a *limited* supply of air or oxygen, carbon monoxide is formed. This gas is an oxide of carbon containing less oxygen than carbon dioxide and having quite different properties. It burns in the air with a characteristic blue flame, forming carbon dioxide. The burning of a

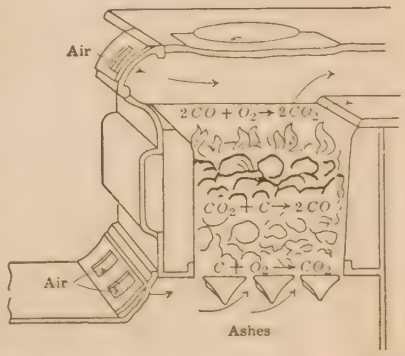


Fig. 51. Formation of the oxides of carbon in a coal fire.

coal fire in a range offers an interesting example of this (Fig. 51). The hot coal on the grate coming in contact with the oxygen of the entering air burns to carbon dioxide. But this gas on passing through the upper layer of coal, where the supply of air is restricted, is reduced to carbon monoxide. At the top of the glowing layer of coal, where abundance of air can find access, the carbon monoxide again burns to carbon dioxide with the well-known blue flame. This carbon monoxide is commonly called **"coal gas"** and is familiar to everyone who has used anthracite (hard) coal.

71. Laboratory method of preparation. We can prepare carbon monoxide by passing carbon dioxide through a tube containing charcoal. The charcoal must be heated red-hot, and the issuing gas must be passed through a solution of caustic soda in order to absorb any of the carbon dioxide which remains undecomposed. The residual gas, carbon monoxide, may be collected over water.

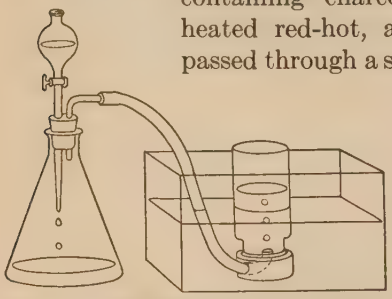


Fig. 52. Preparation of carbon monoxide by action of warm sulfuric acid on formic acid.

An easier method is to treat formic acid with warm concentrated sulfuric acid. The latter causes the decomposition of the formic acid into water and carbon monoxide. The apparatus may be set up as shown in figure 52.

72. Properties of carbon monoxide. Carbon monoxide is a colorless gas, nearly odorless, just a little lighter than air, and very slightly soluble in water. It is one of the gases which it is difficult to liquefy. Its most striking chemical property is the fact that it *burns in air or oxygen with a blue flame, forming carbon dioxide.* It also acts as a **reducing agent** and will reduce metallic oxides, such as copper oxide or iron oxide. In Chapter XXXIII we shall see that the ores of iron are commercially reduced by this gas in a blast furnace.

The reducing action of carbon monoxide may be very well shown by the following experiment. The gas is prepared in the flask *A* (Fig. 53). The bottle *B* contains a little water to wash the gas, and the hard-glass tube *C* holds the black copper oxide, which is heated. The metallic

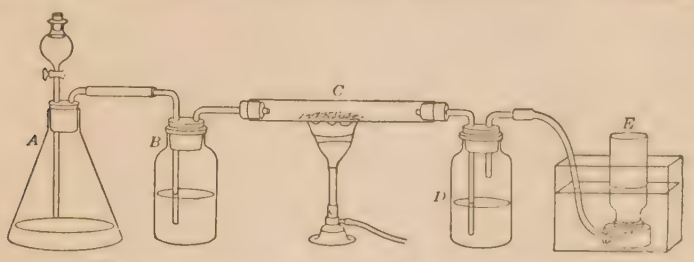


Fig. 53. Copper oxide reduced by carbon monoxide.

oxide is reduced by the gas to reddish metallic copper, and the carbon monoxide is oxidized to carbon dioxide. The presence of this latter gas is shown by the milkiness produced in the limewater in bottle *D*. Any of the unchanged carbon monoxide which passes through is collected over water in *E* and then burned.

The results of this experiment can be briefly stated thus:

$$\underset{\left[\begin{smallmatrix}\text{copper}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{copper oxide}} + \underset{\left[\begin{smallmatrix}\text{carbon}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{carbon monoxide}} \longrightarrow \text{copper} + \underset{\left[\begin{smallmatrix}\text{carbon}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{carbon dioxide}}$$

73. Carbon monoxide a poison. Less than half of one per cent of this gas in the air causes a severe headache, and large amounts may cause death. Every winter there are cases of men who are poisoned while working about an automobile in a small closed garage. The exhaust gases of the gasoline engine contain some carbon monoxide. Sometimes the gas escapes into the room from a coal stove when the draft is not properly regulated; cases of sickness and even of death have resulted from this cause. Illuminating gas, especially that known as water gas, contains carbon monoxide, which is particularly dangerous, since it is itself practically odorless and cannot be recognized in the air. Fortunately illuminating gas generally contains some other substance which has a pronounced smell

and thus gives warning of the presence of the poisonous material. In mine explosions carbon monoxide is always formed. Since birds are very sensitive to this poison, the rescuers often carry canaries with them to warn them of their own danger. In recent years gas masks (Fig. 54) have been provided for miners to use in such emergencies.

Fig. 54. Gas mask for protection against acid fumes, ammonia, carbon monoxide, smoke, and dust.

Carbon monoxide is poisonous because it combines with the red corpuscles of the blood and prevents them from taking up oxygen from the air. Since the life of a person depends on the absorption of oxygen by these blood corpuscles, carbon monoxide causes a sort of internal suffocation, which results in sickness and sometimes death.

74. Composition of carbon dioxide and carbon monoxide. The weights of carbon and oxygen which combine to form carbon dioxide have been determined with great precision. The results of a great number of experiments have shown that the ratio of the weight of carbon to that of oxygen is as 1 : 2.66.

Carbon monoxide has also been very carefully investigated, and it has been found that the ratio of the weight of carbon to that of oxygen is as 1 : 1.33. It will be seen that 2.66 is exactly twice 1.33; that is, the weight of the oxygen combined with the carbon in carbon dioxide is exactly *twice* the amount combined with the carbon in the monoxide. This is a strikingly

simple relationship, and is indicated by the names **di**(two)oxide and **mon**(one)oxide.

75. Law of multiple proportions. The case of carbon monoxide and dioxide is not peculiar. It has been found (§ 57) that hydrogen and oxygen unite in the ratio of approximately 1 to 8 in *water* and of 1 to 16 in *hydrogen peroxide*. In this case weights of oxygen which unite with one gram of hydrogen are in the ratio of 1 to 2. Whenever there is more than one compound containing the same elements, the weights of the one element which are combined with a fixed weight of the other always bear a simple relationship to each other, such as 2 to 1, or 3 to 1, or 3 to 2. This generalization is known as the LAW OF MULTIPLE PROPORTIONS and was first stated by John Dalton in 1804. It may be conveniently expressed in somewhat different language as follows: *When any two elements A and B combine to form more than one compound, the weights of B which unite with a fixed weight of A are in the ratio of small whole numbers.*

This law together with the Law of Definite Composition is the foundation of chemistry. In a later chapter we shall see how Dalton explained these simple generalizations by means of a theory which has made the science of chemistry possible.

SUMMARY OF CHAPTER VI

CARBON DIOXIDE is formed when carbon or carbon compounds burn or decay.

It can be *prepared:*

(1) by burning charcoal in air or oxygen;

(2) by the action of acids on carbonates.

Its *properties:* a colorless gas, slightly soluble in water, and suffocating but not poisonous. It is about 1.5 times as heavy as air. Easily liquefied. Evaporating the liquid produces solid carbon dioxide.

TEST: Does not burn; combines with alkalies and *produces a milkiness in limewater.*

USED in making carbonated beverages such as soda water; in certain types of fire extinguishers; and in ice machines.

CARBON MONOXIDE is formed:

(1) when carbon or carbon compounds burn in a limited supply of air;

(2) by the reduction of the dioxide;

(3) by action of warm sulfuric acid on formic acid.

Its *properties:* a colorless gas and practically odorless, slightly lighter than air, and insoluble in water. Very poisonous. Burns with a blue flame, forming the dioxide. Acts as a reducing agent, taking oxygen from hot metallic oxides, such as copper and iron.

COMPOSITION OF THE OXIDES OF CARBON: Weights of carbon to oxygen

in the dioxide are as 1: 2.66;

in the monoxide are as 1: 1.33.

Weights of oxygen in the two oxides of carbon are as 2 to 1.

LAW OF MULTIPLE PROPORTIONS: When any two elements *A* and *B* combine to form more than one compound, the weights of *B* which unite with a fixed weight of *A* are in the ratio of small whole numbers.

Questions

1. How could you distinguish between carbon monoxide and carbon dioxide?

2. How could you distinguish between carbon monoxide and hydrogen?

3. When alcohol burns, carbon dioxide is formed. What does this show about the composition of alcohol?

4. Does the fact that an acid produces effervescence when added to a material prove the presence of carbon dioxide?

5. How would you test for a carbonate?

6. A beaker of limewater is left standing in the laboratory overnight. The next day the liquid is covered with a white material. Explain.

7. Name two important reducing agents which we have studied thus far.

8. Two samples of illuminating gas contain 6% and 33% of carbon monoxide respectively. Which is the more poisonous?

9. Upon what three properties of carbon dioxide does its use in fire extinguishers depend?

10. How is the quantity of carbon dioxide in the atmosphere kept nearly constant?

11. When the stopper is removed from a bottle of mineral water, it effervesces. How could you prove the bubbles to be carbon dioxide?

12. When carbon dioxide is passed over hot powdered zinc, zinc oxide is formed. What is the other product?

13. The so-called " water-gas " is mainly a mixture of hydrogen and carbon monoxide. Why is water-gas better for heating than for illuminating purposes?

14. What effect would doubling the pressure have upon the solubility of carbon dioxide in water?

15. Carbon dioxide is sometimes spoken of as plant food. Explain.

16. Tobacco smoke is said to contain some carbon monoxide produced by incomplete combustion. How may a smoker avoid this poison?

Topics for Further Study

Heating apparatus in the home. Investigate your kitchen stove. Draw a diagram of it, and indicate what chemical reactions take place at each point. How is your house heated? Make a sketch of the system. Is there any danger of carbon monoxide escaping into the rooms? What might happen if the lining of the fire box in a hot-air furnace were defective?

Coal-mine explosions. What is the cause of explosions and fires in coal mines? What steps have been taken by the mining companies and the government to reduce the danger from this source? (Consult pamphlets issued by the Bureau of Mines.)

CHAPTER VII

NITROGEN AND THE ATMOSPHERE

Importance of nitrogen — preparation from air and by decomposition of compounds — properties. Air, a mixture — liquefaction — commercial uses of nitrogen. Rare gases in air — use of helium. Composition of air — rôle of carbon dioxide in nature — impurities in " bad air " — fresh air.

76. Importance of nitrogen. We have already learned (Chapter III) that about one-fifth of the air is oxygen; nearly all the remaining gas is the element called nitrogen. Combined with other elements it is present to a limited extent in certain mineral deposits, such as saltpeter. *Nitrogen compounds are essential to life*, and are present in all living matter and in its decomposition products. In fact, a valuable constituent of our food is protein material, which contains a large percentage of chemically combined nitrogen. Soils and fertilizers serve as food for plants very largely in proportion to the percentage of nitrogen which they contain. Modern explosives, such as guncotton, nitroglycerin, and dynamite, are unstable nitrogen compounds. Such nitrogen compounds as ammonia and nitric acid play a very important rôle in the industries of a nation. The compounds of nitrogen are so important that we shall consider them in separate chapters (XX, XXI), confining our attention at present to the element itself and to the air.

77. Preparation from air. As has been said, Lavoisier found that air contains oxygen, which may be removed by causing it to combine with mercury. We can, however, remove the oxygen much more quickly by burning phosphorus, and can thus obtain fairly pure nitrogen.

We place a piece of phosphorus (wiped dry) in a porcelain crucible which rests on a cork floating on the surface of a pan of water. It is ignited with a hot wire, and a jar is placed over the burning solid, as shown in figure 55. The phosphorus burns in the confined air in the jar and forms the same dense white smoke as when burned in pure oxygen. We then allow the jar to stand for a short time so that it may cool and the fumes, which consist of very fine, solid particles of oxide of phosphorus, may dissolve in the water. It will be noticed that the *water has risen in the jar about one-fifth*, taking the place of the oxygen. If we now introduce a lighted taper or candle into the gas in the jar, we find that the flame is at once extinguished. The residual gas will not support combustion.

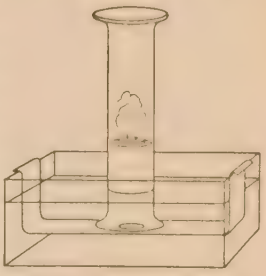


Fig. 55. Removing oxygen from air by burning phosphorus.

This inert gas was called by Lavoisier azote, which signifies that it is incapable of supporting life. Later it was named nitrogen because of its presence in saltpeter, or niter. Animals cannot live in nitrogen, not because it is in any way poisonous, but simply because animals *must* have free oxygen. They die of suffocation in nitrogen just as they drown in water.

78. Preparation of pure nitrogen. Until 1894 it was thought that pure nitrogen could be prepared from air by removing all the oxygen and the small amount of carbon dioxide that is always present. But it has been found that such nitrogen contains about one per cent of impurities, which are the so-called " rare gases " (argon, helium, neon, krypton, and xenon).

Pure nitrogen can be most conveniently prepared in the laboratory by heating a compound of nitrogen called ammonium nitrite. This decomposes into nitrogen and water. Inasmuch as ammonium nitrite is unstable, we use a mixture of sodium nitrite and ammonium chloride. The reaction, however, is complicated, and we need not consider it at this point.

The chief source of nitrogen for commercial purposes is liquid air. This liquid is allowed to evaporate and then, since the nitrogen is more volatile (that is, boils at a lower temperature), it passes off first, leaving the oxygen behind. Both products (the oxygen and nitrogen) are commercially valuable.

79. Properties. Nitrogen is like oxygen and hydrogen in having neither color, taste, nor odor; but in other respects it is very different. For instance, it does not burn and does not support combustion. In fact, its only characteristic which can be easily shown is that it does not readily enter into chemical reactions. It does, however, unite, although slowly, with certain other elements, provided these are heated to the proper temperature. It unites with red-hot magnesium, forming a compound of magnesium and nitrogen called **magnesium nitride.** When electric sparks are passed through a mixture of nitrogen and oxygen, the nitrogen will combine with oxygen to form **oxides of nitrogen.** In the presence of a suitable catalyst it will also combine with hydrogen at a moderately high temperature to form ammonia, which is a gaseous compound of nitrogen and hydrogen. Although these last two reactions take place only with difficulty, yet they have recently become of great importance because they enable us to transform the free nitrogen of the air into compounds of nitrogen. Compounds of nitrogen are essential to plant life, and their preparation from the nitrogen of the air is a modern chemical problem of enormous importance.

80. Air a mixture. The oxygen and nitrogen in air are not chemically combined. Air is only a mixture of these two gases and very small amounts of some others. There are a number of pieces of evidence which clearly show that *air is a* ***mixture*** *and not a chemical compound.*

(1) In the first place, pure nitrogen and oxygen can be mixed together to form an " artificial air " which is almost identical with ordinary air. There is no heat evolved or other sign of a chemical reaction

when these gases are mixed. The proportions of the gases in this "artificial air" may be varied very considerably without appreciably affecting the chemical properties of the product. If the oxygen and nitrogen were chemically combined, there would be one definite proportion in which they would unite.

(2) In the second place, water will dissolve air; if we expel this air from water by boiling and then analyze it, we find that it contains nearly twice as much oxygen as the original air. Oxygen is more soluble in water than nitrogen, and therefore relatively more of it dissolves. If the oxygen and nitrogen were combined, the dissolved gas would have the same composition as the air.

(3) Finally, we can separate air into its components by a purely physical process. This is done by liquefying the air and then carefully boiling off the more volatile nitrogen. If air were a compound, it would all boil at the same temperature.

81. Liquefaction of air. There is a definite temperature below which a gas must be cooled before it can be liquefied (§ 40). This is known as the **critical temperature,** and is different for different gases. In the case of both oxygen and nitrogen the critical temperature is so low that it is impossible to liquefy these gases at ordinary temperatures, however much we compress them. To liquefy air *we must cool it to a very low temperature as well as subject it to a high pressure.* This is done on a large scale in an apparatus which is constructed as in figure 56.

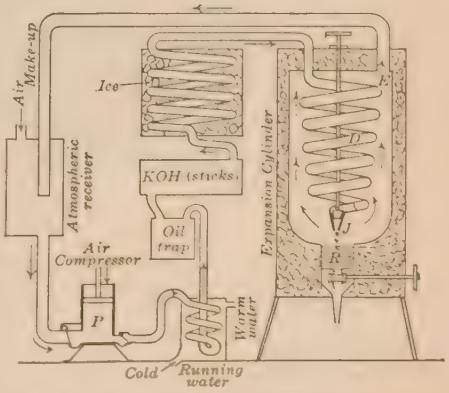


Fig. 56. Diagram of essential parts of liquid-air machine.

This diagram shows only the essential parts of the apparatus. The air is compressed by a pump *P*, and the heat produced by the compression is removed by passing the air through cooling coils. The compressed

air is made to expand rapidly by allowing it to issue from a very small jet *J* into an expansion cylinder kept at a lower pressure. As the air passes through this jet and expands, it absorbs a great deal of heat. *When a gas is compressed it gives out heat, and when a gas expands it absorbs heat.* This heat is removed from the gas, which is under pressure, by causing the expanded gas to flow back over the outside of the high-pressure pipe *D* through the cylinder. The cold

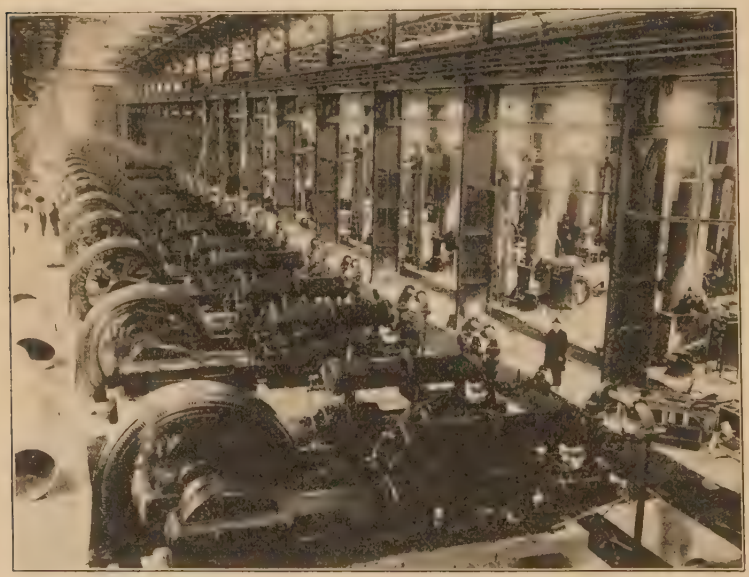


Fig. 57. Air compressors for producing liquid air, from which nitrogen is prepared.

expanded air is then compressed again and the process continued. Finally the gas is cooled so low by its own continued expansion that it liquefies and is collected in vessel *R*, from which it can be drawn off as needed.

We have just seen that *air*, like many other gases, *is liquefied by the combined effect of pressure and low temperature*. Liquid air is really only a mixture of liquid nitrogen (boiling point, − 195.7° C.) and liquid oxygen (boiling point, − 182.9° C.).

It is commercially possible to separate the more volatile nitrogen from the oxygen. In this way oxygen is manufactured for industrial use and is compressed into steel tanks. Nitrogen is also prepared commercially (Fig. 57) by the same process.

82. Experiments with liquid air. Liquid air is coming to be a commercial article which can be purchased in many places. If poured into an ordinary glass vessel, it quickly absorbs enough heat through the glass to cause it to boil away completely. It can be kept or transported only in an especially constructed apparatus called a Dewar flask (Fig. 58). This flask consists of two glass vessels, one inside the other, the intermediate space being exhausted with a vacuum pump. The liquid air in such a flask is thus surrounded by a vacuum, which conducts heat very slowly, and consequently the liquid will not readily evaporate. To decrease the evaporation still further, the flasks are often silvered; this causes the heat to be reflected away from the exterior. The flask is also carefully packed in a basket with some non-conductor, such as felt, to prevent the inflow of heat from the outside.

Fig. 58. Dewar flask.

Ordinary materials manifest peculiar properties when cooled to the temperature of liquid air. For example, if a small rubber ball is immersed in liquid air and then dropped on the floor, it breaks into many pieces as if made of glass. In the same way a rubber tube which conducts liquid air soon becomes so brittle that it breaks to pieces. Flowers and grass are frozen solid by immersion in liquid air and are very brittle when removed. If a burning stick is plunged into liquid air it keeps on burning. A flame of hydrogen or coal gas dipped under the surface of liquid air goes on burning, and the water which is formed freezes.

83. Uses of nitrogen. Free nitrogen is used to fill certain kinds of electric-light bulbs. On account of its inertness it does not attack the white-hot filament in the lamp. When mercurial thermometers are to be used at temperatures from 300° to 500° C., the space above the mercury in the stem is filled with nitrogen under pressure. In this way the mercury is prevented from boiling, even at temperatures above its normal boiling point (357° C.). Free nitrogen is also used in the

manufacture of nitric acid, ammonia, and certain nitrogenous fertilizers (§ 253).

84. Rare gases. Five elements — argon, neon, helium, krypton, and xenon — occur in the air in very small quantities. Argon, which is the most abundant of these, occurs to the extent of only 0.94 of one per cent by volume. The other four together constitute less than 0.002 per cent of the air. **Argon** was first discovered in 1894 by Sir William Ramsay (Fig. 59) and Lord Rayleigh; they removed all the oxygen and nitrogen from air by chemical methods, a very long and tedious process. It has since been found possible to prepare argon more conveniently by the liquefaction of air. The other elements are present in such minute amounts that their isolation and study was a matter of very long and painstaking research.

Fig. 59. Sir William Ramsay (1852–1916). An English chemist who discovered the rare gases in the air.

These five elements are all remarkably inert substances; it has not yet been found possible to make them enter into any chemical reaction. For this reason argon is sometimes used in the place of nitrogen for filling electric-light bulbs, being prepared commercially by the liquefaction of air.

85. New uses for helium. Since 1918 helium has come to be a substance of practical importance. Next to hydrogen it is the lightest known gas, being about seven times lighter than

air. It is noninflammable and therefore an ideal substance for filling balloons and dirigibles (Fig. 60); for most of the serious accidents which have occurred in the past have been due to the hydrogen's catching fire. Under the stress of the World War the production of helium for aëronautical purposes has been accomplished on a large scale, and the use of this

Official Photograph, *U.S. Navy.*

Fig. 60. Non-rigid dirigible C–7, on the occasion (Dec. 1921) of the first public balloon flight ever made with *helium*.

gas will be of great importance in the future development of balloons and lighter-than-air airships. Certain natural gases which issue from the ground in Texas contain as much as 1 per cent of helium. By a process of liquefaction helium, which boils at the very low temperature of − 269° C., can be separated from the other gases.

Formerly helium was so much of a laboratory curiosity that it cost about $1700 per cubic foot, and probably not more than

100 cubic feet of the gas had ever been collected by anyone. At the close of the World War the United States government built a large plant which can produce about 50,000 cubic feet per day at a cost of about 3 cents per cubic foot.

Helium is finding an important use in reducing the hazard of deep-sea diving and caisson work. A synthetic atmosphere in which helium takes the place of the nitrogen of the air reduces the liability of workers to caisson sickness when they come out from the high-pressure atmosphere in which they work.

86. Composition of the air. Samples of air taken in the open country have all been found to have the same composition, except for the content of water vapor. The composition of a sample of dry air is as follows:

100 volumes of air contain

Nitrogen	78 volumes
Oxygen	21 volumes
Argon	0.94 volumes
Carbon dioxide	0.04 volumes
Helium, neon, krypton, xenon	traces

In cities and in poorly ventilated places the composition of the air may be very different. The changes in composition of the air which occur in such regions are, however, insignificant when compared with the large bulk of air which surrounds the earth. This great ocean of gas is constantly being stirred by the winds and air currents, and thus its composition, if taken in the open country, is always constant.

87. The rôle of carbon dioxide in the air. Although the amount of carbon dioxide in the air is usually very small indeed, it plays a most important rôle. This gas is pouring into the atmosphere from every chimney and smoke stack; it is produced wherever carbon compounds burn or decay; and is being exhaled by every living organism. On the other hand, all green

plants absorb from the air carbon dioxide, which unites in the leaves with the water which has been absorbed from the soil by the roots. The products of this wonderful synthesis are starch and sugar (which are compounds of carbon, hydrogen, and oxygen), and oxygen, which is set free. We have seen (§ 63) the bubbles of oxygen rising from plants which were growing under water.

The chemical change which converts inorganic material (carbon dioxide and water) into living matter *can take place only in the sunlight*, and is brought about by the aid of the green coloring material in the leaves.

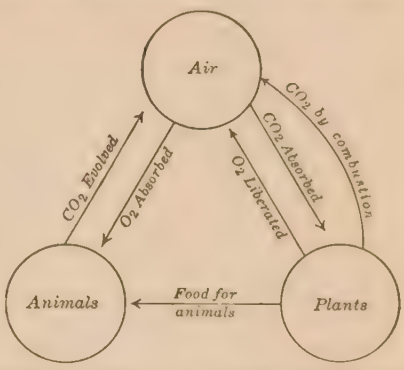


Fig. 61. Diagram to show the cycle of carbon and oxygen.

Thus it will be seen that animals and plants are complements of each other as regards the supply of oxygen and carbon dioxide in the air. The plants remove the carbon dioxide from the air and convert it into compounds, which in turn become food for the animals. The animals burn this food and exhale carbon dioxide (Fig. 61).

88. Impurities in the air affecting human comfort. We are all familiar with the so-called "bad air" which is found in overcrowded, poorly ventilated rooms, and the disagreeable feelings which this "bad air" produces. It was formerly thought that the chief factor in air which influenced human comfort was carbon dioxide, since the carbon dioxide content is always high in crowded, stuffy rooms and the oxygen content lower than normal. But this view has been shown to be erroneous. It is true that healthful air must contain a certain minimum of oxygen and that one can suffocate in an atmosphere

containing too much carbon dioxide. Yet the amount of carbon dioxide which is found in even the worst ventilated rooms is far below this amount. *The chief factors which really determine whether or not air is pleasant to breathe are:* (1) **moisture,** (2) **temperature,** (3) **dust,** (4) **minute amounts of complex compounds exhaled by men and animals.**

The first two factors are closely associated. The human body is normally at a constant temperature of 98.6° F. (37° C.), and this temperature is regulated by the evaporation of water from the surface of the body. If the surrounding atmosphere is particularly moist, this evaporation proceeds with difficulty, and the regulation of the body temperature is correspondingly difficult. Very hot, moist air is one of the most disagreeable atmospheres in which to work. Similarly, if the air is too dry the evaporation from the body proceeds too rapidly, and the normal physiological activities are upset. A proper control of the moisture content (called **humidity**) is one of the essentials for comfort. Another important factor is, of course, the proper regulation of the **temperature.**

The presence of **dust** in the air causes a great deal of discomfort. Air in cities and in crowded rooms contains large amounts of dust, which not only irritates the respiratory organs but contains disease-producing bacteria. Air in the country after a good rain is relatively free from dust, and is always more pleasant to breathe than the dusty air of the city street after a long period of drought.

The fourth factor which affects air is noticeable only in poorly ventilated rooms containing many people. The human body gives off very small amounts of substances which cause the air to have a disagreeable physiological effect. These minute impurities probably affect people by their disagreeable odor and possibly also because they are actually poisonous to the human system. Whatever the reason, they cause the air of a crowded room to produce drowsiness, general discomfort, and even severe headaches.

The impurities and the dust may be removed from the air by washing it with a sort of shower bath of water. Very successful systems of ventilation have been installed in which the air is drawn out of the rooms, passed through a washer, partially dried, and sent back into the rooms again. Although the carbon dioxide content in such air may be relatively high, it produces no disagreeable effects. This system of ventilation is superior to that which merely introduces fresh air from the outside, because it does not necessitate the heating of

large amounts of cold air. A great saving in the fuel used for heating the building thus results.

89. How to get fresh air. Because the atmosphere in the country is really clean, it is well for everyone to *live as much as possible in the open air*. Since, however, a great deal of the world's work must be done indoors, it is important that we take every precaution to ventilate our houses properly. Some people have thought that night air is injurious, but a careful study shows that night air is the same as that which we breathe during the day. In fact, the proper ventilation of a sleeping room is one of the first requirements for good health. Since the exhaled air is usually warmer and lighter than the inhaled air, it rises to the top of the room. Therefore it is better to open a window *at the top* to let the hot upper air out and also *at the bottom* to admit the fresh air (Fig. 62). Of course, this does not mean that one should sleep in a strong draft. In many places it is feasible to sleep out-of-doors on a sleeping porch and so to secure perfect ventilation.

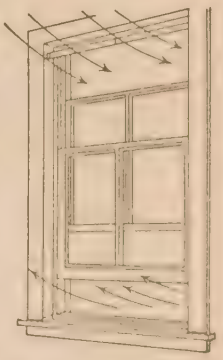


Fig. 62. Ventilation of a room by opening the window at top and bottom.

SUGGESTION

For further rules about healthful living, read Fisher and Fisk's *How to Live*. — Funk & Wagnalls Co.

SUMMARY OF CHAPTER VII

ELEMENTARY NITROGEN forms about *four-fifths of the air*. **Nitrogen compounds are *essential* to life and important industrially.**

PREPARED from the air by burning out the oxygen with phosphorus or with red-hot copper; this is sufficiently pure for most purposes. Commercial nitrogen is prepared from liquid air by evaporation.

PURE NITROGEN is prepared by heating ammonium nitrite (sodium nitrite and ammonium chloride), which gives water and nitrogen.

PROPERTIES: nitrogen is an inert substance. It is a colorless, odorless, tasteless gas; does not burn; does not support combustion or respiration; is not poisonous. It does not easily unite directly with other elements. At high temperatures it combines with a few metals such as magnesium, and also with oxygen and hydrogen.

AIR IS A MIXTURE, NOT A COMPOUND. It is essentially composed of nitrogen, oxygen, and argon with varying amounts of water vapor, carbon dioxide, and dust.

AIR CAN BE LIQUEFIED and separated into its components by allowing the more volatile nitrogen to boil off first.

ARGON occurs in air to the extent of nearly one per cent by volume. There are traces of four other rare gases, which cannot be made to combine with any other elements. Argon is used for filling electric-light bulbs.

HELIUM is one of the rare gases; it can be made commercially by liquefying certain natural gases. It is noninflammable and seven times lighter than air. Used in airships.

CARBON DIOXIDE is introduced into the air by combustion and respiration. It is removed by green plants, which get all their carbon from the carbon dioxide in the air and produce oxygen. This balance of plant and animal life keeps the amounts of oxygen and carbon dioxide in the air constant.

The *chief factors* in the air which affect *human comfort* are (1) moisture, (2) temperature, (3) dust, (4) small amounts of impurities given off by the human body. To get as much fresh air as possible — work, play, and sleep out-of-doors.

Questions

1. How would you distinguish between nitrogen and carbon dioxide?
2. Of what use is the carbon dioxide in the air?
3. Why will an animal die in nitrogen gas?

4. Why are traces of nitrogen compounds found in the air after a thunderstorm?

5. Every ton of coal burned produces about 3 tons of carbon dioxide. Why does the composition of the air vary so little?

6. If a teakettle containing liquid air is placed on a cake of ice, the liquid boils vigorously (Fig. 63). Explain.

7. Why do we not put a tight stopper in a bottle containing liquid air?

8. How would you prepare a sample of air which is free from water vapor and carbon dioxide?

9. If air has a definite composition, why is it not considered a compound?

10. State three ways in which oxygen can be removed from air.

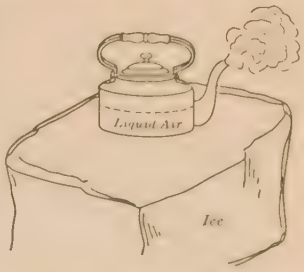


Fig. 63. Liquid air in the teakettle boils on a cake of ice.

11. Why are there so few nitrogen compounds among the minerals?

12. What are the principal objections to dust in the air we breathe?

13. How may one increase the humidity of the air in a room?

14. Why do not green plants produce as much oxygen at night as during the day?

15. What relief does an electric fan in a room offer on a hot day? Explain.

16. Why does the carbon dioxide not form a layer at the bottom of a room?

17. What components of the air are always present but vary in amount?

Topics for Further Study

Ventilation. Investigate the ventilation of the classroom. The air currents may be observed by means of lighted bits of paper. Notice the effect of opening and closing the windows. What are the modern methods of ventilating schoolrooms, theaters, and public halls? Why is it not necessary to have a ventilating system in a dwelling-house? What methods can be used for regulating the temperature and the humidity?

Discovery of argon. What facts led to the discovery of this element? How was free argon prepared by Ramsay? Why was this component of the air so long overlooked? (Tilden's *Chemical Discovery and Invention in the Twentieth Century.*)

CHAPTER VIII

DALTON'S THEORY OF ATOMS AND MOLECULES

Three laws — conservation of matter, constant and multiple proportions — facts and theories — Dalton's theory of atoms — explanation of facts — atoms and molecules — physical and chemical changes — value of atomic theory.

90. Review of the three fundamental laws. In all our study of chemical substances and their changes we find that matter is indestructible; that is, *the sum of the weights of the substances which take part in a chemical change is equal to the sum of the weights of the products formed* (Law of Conservation of Matter).

We have also seen that one of the most important characteristics of a chemical compound is expressed by the Law of Definite Composition: *the weights of the elements which combine to form a given compound are always in the same definite relation.* That is, the composition of a chemical compound never varies.

We further saw that *when two elements combine to form more than one compound, the weights of one element which unite with a fixed weight of the other are in the ratio of small whole numbers.* This is the Law of Multiple Proportions. These laws are the general expressions of a vast number of well-established facts.

91. Facts and theories. Whenever we are confronted with a series of facts, we are prone to ask ourselves the question, Why are these facts so? To explain and account for **facts** chemists have adopted certain **theories.** It is worth while to see just what the difference is between laws and theories. A **law** may be defined as a generalization based on experimental facts; it is a convenient method of summarizing the results of a large number of investigations. A ***theory*** *is a sort of scientific guess,*

or hypothesis, which we make in order to explain the facts. If the hypothesis fits all the facts, it is considered a satisfactory theory so long as no new facts are discovered which disagree with it; but if fresh facts are found out which will not harmonize with the theory, it must be given up and a new one proposed.

A theory always starts with certain assumptions which we cannot test experimentally. Beginning with these assumptions, we reason that so and so must be true. The more closely these conclusions fit the known facts the more likelihood there is that the theory is correct. We cannot, however, say that the theory is proved, but merely that it is probably true.

Fig. 64. John Dalton (1766–1844). An English schoolmaster and chemist who introduced the atomic theory.

92. What is Dalton's theory of atoms? The early Greek philosophers (about 300 B.C.) believed that all matter was composed of very minute particles, which could not be further subdivided. These ultimate bits of matter they called **atoms**. The ancient thinkers, however, had such a meager knowledge of natural science that they could not make use of this theory to explain natural phenomena. John Dalton, an English schoolmaster (Fig. 64), in 1808 put forward a theory which explained very simply the Law of Definite Composition and Multiple Proportions. Dalton, like the Greeks, assumed that all matter was composed of very minute particles, which he also called **atoms**; but aside from this fundamental assumption,

his views were quite different from those of the early philosophers. His contribution, generally known as the **atomic theory,** has been adopted to explain the facts about chemical compounds, and it may therefore justly be said to be the most comprehensive and useful theory in modern chemistry.

Dalton made the following assumptions:

(1) Matter is made up of small particles called atoms.

(2) All the atoms of a given element are exactly alike in size and weight,* but differ in these respects from the atoms of every other element.

(3) Atoms can unite with other atoms and hold them by a force called chemical affinity; it is this union of atoms which produces chemical compounds.

(4) Atoms cannot be divided, and therefore only whole atoms unite with each other.

93. How this theory helps us to understand the facts. *First,* as to the fact that compounds always have a definite composition. According to this theory we assume that a compound is due to a union of atoms of different elements. For example, in carbon monoxide one atom of carbon unites with one atom of oxygen, forming a group of two atoms. Since all the oxygen atoms have exactly the same weight and the carbon atoms also have each a fixed weight, any sample of carbon monoxide will have a definite composition. This is the Law of Definite Composition.

Second, as to the Law of Multiple Proportions. It is conceivable that a carbon atom might unite with two atoms of oxygen instead of only one. An entirely different compound would result; in each group there would be one carbon atom and *two* oxygen atoms. That is, there would be twice as much oxygen combined with carbon as in the first case. Carbon dioxide is, in fact, just such a substance; it contains twice as much oxygen as carbon monoxide. In carbon dioxide we imagine that every atom of carbon is united with two atoms of oxygen.

*Aston has recently proved that this is not always true (§ 224).

Finally, as to the Law of Conservation of Matter. We assume that in a chemical change the atoms are redistributed, but that none are produced or annihilated. The sum of the atoms of the substances which take part in a chemical reaction must equal the sum of the atoms in the products, since none are lost in the change. This simply means that matter is indestructible.

94. Atomic weights of the elements. *The smallest part of an element which can take part in a chemical change is called an* ***atom.*** Since the atoms of the elements are so very small, we shall not attempt to use the actual weights of single atoms, but rather the *relative weights* of their atoms. The oxygen atom is taken as the standard because it combines with so many elements and its value is fixed as 16. On this basis the hydrogen atom is slightly more than 1 (1.008). *The atomic weight of an element is the weight of an atom as compared with the weight of one atom of oxygen taken as 16.*

The numbers which are now accepted by chemists as representing the atomic weights of the elements are given in the table in the back of the book. It will save time if we become familiar with the approximate atomic weights of some of the commoner elements. In this table we see that the atomic weight of carbon is 12 and of oxygen is 16. Therefore in carbon monoxide we should expect 12 parts by weight of carbon to unite with 16 parts by weight of oxygen; in other words, the ratio of carbon to oxygen would be as 1 : 1.33, which corresponds to the results of the chemical analysis of carbon monoxide. The fact is, as we shall see later (Chapter XIX), that the numbers in the table are derived from the relative combining weights of the elements in compounds. These weights are determined by very precise analysis of the compounds. Therefore the table of atomic weights represents certain chemical facts in regard to the elements which are quite independent of any theory.

95. Molecules of gases. We have already seen in Chapter IV that a gas is assumed to be composed of a vast number of minute particles called **molecules.** In most common gases, such as oxygen, nitrogen, and hydrogen, each molecule is made up of two atoms held together in chemical combination. In the case of a compound such as carbon monoxide the carbon and oxygen atoms are joined together in groups; these groups of atoms are molecules. A great number of such molecules make up the gas which we recognize as carbon monoxide. Thus, in certain elementary gases, such as oxygen, hydrogen, and nitrogen, the molecule is composed of two atoms of the *same* element; in a compound the molecule is composed of two or more atoms of *different* elements. For example, a molecule of water is composed of an atom of oxygen and two atoms of hydrogen. There are a few cases, such as helium and mercury vapor, where the molecule of the gas consists of a single atom; these gases are said to have *monatomic* molecules.

96. Physical and chemical changes. When a gas, such as air, is liquefied, we think of the molecules as coming closer together in the space they occupy; and again, when the liquid is frozen, we imagine the molecules as coming still closer together so that they attract each other with considerable force. But in all these states of matter we conceive of the molecules as vibrating, and the temperature of a body as an outward indication of the rapidity of this vibratory motion. *These changes which affect the molecule as a whole we call* ***physical changes.***

If, however, we disturb the composition of the substance by breaking through the force which united the atoms, we produce a **chemical change.** For example, when we separate the constituent atoms in water and obtain hydrogen and oxygen, which are both entirely different in their properties from the original water, that is a chemical change.

We may define *an* ***atom*** *as the smallest particle of an element which can take part in a chemical change.* We may also define *a*

molecule as the smallest particle of matter which can exist in a gaseous state.

97. Atomic Hydrogen. Ordinary gaseous hydrogen is in the form of molecules. It has recently been discovered that the hydrogen molecule may be partially broken down (dissociated) into hydrogen atoms by subjecting the gas to the extraordinarily high temperatures of the electric arc (Fig. 65). This dissociation of the molecule absorbs tremendous amounts of energy, which are liberated again when the hydrogen atoms combine to form hydrogen molecules:

$$\text{hydrogen molecules} + \text{energy} \rightleftharpoons \text{hydrogen atoms}$$

Practical advantage has been taken of this atomic hydrogen in producing an intensely hot flame for welding metals. A stream of hydrogen gas is blown over an electric arc, where the dissociation takes place. A short distance from the arc the atoms recombine to form molecules, producing *locally* a very high temperature (about 4000° C.). Such a flame of atomic hydrogen as used in welding is shown in the frontispiece. It must be remembered that this "atomic flame" involves no oxygen; the molecular hydrogen burns in the air in the usual way forming an *outer flame*, the temperature of which, however, is relatively low. Because of the reducing action of atomic hydrogen, this new type of welding is particularly useful, since any film of oxide is reduced to the metal.

Fig. 65. An arc welding torch producing atomic hydrogen. The electrodes are tungsten rods. A jet of hydrogen is directed into the arc.

98. Value of the atomic theory. If the theory of atoms is merely an hypothesis about the atoms, which are so small that we cannot see them, why study the theory at all? It is an interesting fact that, although it is more than a hundred years old, it has never been replaced by a better one. Chemists generally agree that it does explain satisfactorily the facts regarding chemical combination, and that it has done more than any other theory for the advancement of the physical sciences. In recent years an abundance of new experimental evidence has been found, which we cannot here describe in detail since it involves considerable mathematical physics. The atomic theory has been so strengthened and extended by all this work that scientists have come to believe in the existence of atoms and molecules with as much certainty as is possible about things which we cannot see by direct observation.

SUMMARY OF CHAPTER VIII

THE ATOMIC STRUCTURE of matter was first suggested by early Greek philosophers. John Dalton in 1808 used it as a basis for a theory which explained the Laws of Definite and Multiple Proportions.

DALTON'S THEORY assumes the following:

(1) All matter is composed of atoms.

(2) All atoms of a given element are alike.

(3) Atoms can unite with and hold other atoms by reason of a force called chemical affinity.

(4) Atoms are indivisible, and therefore only whole atoms can unite with one another.

AN ATOM is the smallest particle of an element which can take part in a chemical change.

A MOLECULE is the smallest particle of matter which can exist in a gaseous state.

A LAW is a generalization of experimental *facts;* a *theory* involves certain assumptions from which certain conclusions may be drawn to explain a series of experimental facts. An

hypothesis **is a scientific guess which, if satisfactory, may become a theory.**

THE ATOMIC THEORY is still a theory, but science has recently developed considerable evidence which makes the reality of atoms and molecules extremely probable.

Questions and Problems

1. Show how the Law of Conservation of Matter applies to the decomposition of red oxide of mercury.

2. Show how the Law of Definite Composition applies to the composition of water.

3. Sulfur dioxide is 50% sulfur and 50% oxygen. Sulfur trioxide is 40% sulfur and 60% oxygen. Show how these facts illustrate the Law of Multiple Proportions.

4. Copper and oxygen unite to form two compounds having the following percentage composition:

	I	II
Copper	79.9	88.8
Oxygen	20.1	11.2

Show that we have here a case of multiple proportions.

5. State in your own words the four assumptions which Dalton made in his atomic hypothesis.

6. What is the difference between an hypothesis and a theory?

7. What is the difference between a natural law and a state law?

8. What theory accounts for the effects of temperature and pressure upon the volumes of gases?

9. What is meant by the terms: (*a*) atom of an element, (*b*) molecule of an element, (*c*) molecule of a compound?

10. Classify the following as either physical or chemical changes: (*a*) the burning of wood, (*b*) the evaporation of gasoline, (*c*) the dissolving of sugar in water, (*d*) the souring of milk, (*e*) the melting of butter, (*f*) the decay of food, (*g*) the explosion of dynamite.

Topic for Further Study

Science in ancient Greece and Rome. Why did not the early Greek philosophers apply their idea of the atomic theory to explaining chemical facts? Were they interested in chemistry and physics? (Moore's *History of Chemistry*, and Sedgwick and Tyler's *Short History of Science*.)

CHAPTER IX

SYMBOLS, FORMULAS, AND VALENCE

Meaning of symbols and formulas — writing formulas — valence — graphical representation — table of valences — variable valence.

99. Chemical symbols. Chemists have found it convenient to represent the various elements by the symbols which are given in the table on the back cover. These symbols were introduced by the Swedish chemist, Berzelius (Fig. 66), and are usually the first letter, capitalized, of the names of the elements. Examples are C for carbon, H for hydrogen, O for oxygen, and S for sulfur. In a few cases where two or more elements have the same initial letter, another letter that is prominent in the name is added, but not capitalized ; such as Cl for chlorine, Br for bromine, Si for silicon, and Mg for magnesium. In other cases, such as the metals known to the ancients, the symbol is taken from the Latin name; thus, Cu stands for copper (*cuprum*), Fe for iron (*ferrum*), Ag for silver (*argentum*), and Au for gold (*aurum*).

Fig. 66. Johann Jacob Berzelius (1779–1848). The most distinguished chemist of his day. Introduced the modern symbols.

It will be well to learn the symbols of the common elements as we study them.

100. What does a symbol mean? These symbols are not used *merely* as shorthand signs, but each one stands for *an atom* of the element. Thus, the symbol O stands for one atom of oxygen, and the symbols H, N, Na, Fe represent one atom of hydrogen, nitrogen, sodium, and iron, respectively, and not merely these substances in general. More exactly, then, they are *atomic symbols*, and not merely abbreviations of the names of the elements.

We have also seen that *each atom has a perfectly definite weight*, and so the symbol means not only the element but a definite quantity of the element. O always means 16 parts by weight of oxygen, C always means 12 parts by weight of carbon, and H always means 1.008 parts by weight of hydrogen.

When we know how many atoms of an element go to make up a molecule of that element, we can express this knowledge very briefly by symbols with small subscripts placed after them. Presently we shall show that each molecule of hydrogen, oxygen, nitrogen, chlorine, and some others consists of two atoms; this fact is represented by the symbols H_2, O_2, N_2, Cl_2, respectively. The symbol H_2 thus means *one molecule of hydrogen*.

101. Chemical formulas. We may represent the composition of any compound by means of these symbols. This is done by placing side by side the symbols for the various elements in the compound. For example, a molecule of sodium chloride (common salt) is made of one atom of sodium (Na) and one atom of chlorine (Cl), and is represented by the united symbols of the two elements, NaCl. Such an arrangement of symbols representing a compound is called the formula of that compound.

When the molecules of a compound contain more than one atom of any particular element, this fact, as we have said, is expressed by placing small numbers immediately after and a little below the symbol of that element. Thus, H_2O is the for-

mula for one molecule of water, a compound containing two atoms of hydrogen and one atom of oxygen. Very often it is necessary to indicate a group of atoms (radical) in a molecule which behave in many reactions like a single atom. Parentheses are used for this purpose. Thus, a molecule of calcium hydroxide (limewater) may be represented by $Ca(OH)_2$, which indicates a molecule containing one atom of calcium, two atoms of oxygen, and two atoms of hydrogen.

When we wish to indicate more than one molecule of any substance, we place large numerals before the symbol or formula. Thus, $2\ O_2$ means two molecules of oxygen, and $5\ H_2O$ means five molecules of water.

102. What does a formula stand for? It is very important that we understand the full meaning of a formula. For example, the formula for sulfuric acid is H_2SO_4, which means:

(1) one molecule of sulfuric acid;

(2) composed of two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen;

(3) 2 parts by weight of hydrogen, 32 parts by weight of sulfur, and 4×16 or 64 parts by weight of oxygen;

(4) $2 + 32 + 64$ or 98 parts by weight of sulfuric acid.

Questions and Problems

1. What is the distinction between a symbol and a formula? Illustrate each.

2. Give the symbol of each of the following elements: sodium, sulfur, manganese, magnesium, mercury, potassium, phosphorus, lead, platinum, and iron.

3. Name the elements which correspond to the following symbols: Ag, Sn, W, Ni, Au, Cu, A, Ra, As, and Al.

4. State the facts expressed by the formulas: $CuSO_4$; $3\ NaCl$; $2\ H_2O$; P_4; and $Ba(OH)_2$.

5. State the meaning of each figure and letter in the following formulas: $2\ H_2SO_4$; $10\ H_2O$; $(NH_4)_2SO_4$; $Fe_2(SO_4)_3$.

103. Writing chemical formulas. Valence. In our study of compounds we shall notice that the various elements differ

greatly from one another in the number of hydrogen atoms with which they will combine. This fact is illustrated in these compounds:

HCl	H_2O	NH_3	CH_4
hydrogen chloride	water	ammonia	marsh gas

Thus, an atom of chlorine combines with *but one* hydrogen atom, an atom of oxygen with *two*, an atom of nitrogen with *three*, and an atom of carbon with *four*. We call *this property of an element its* ***valence***. *The valence of an atom is that whole number which expresses how many hydrogen atoms its atom can hold in combination or can replace in a reaction.* For example, the valence of chlorine is one, of oxygen two, of nitrogen three, and of carbon four.

104. Graphical representation. The valences of elements do not tell us anything about the reasons why certain elements unite and certain others do not. They merely tell us the number of hydrogen atoms with which elements can combine. Furthermore, we do not know in what way the elements are actually joined to one another; but our rules of valence tell us how many atoms will be united in a given compound. We can picture this graphically by supposing that each atom has a certain number of **bonds** which enable it to join with some other atom or atoms. We are quite certain, of course, that the actual way in which atoms are linked is different from that represented in figure 67, but we may use this method in order to visualize the conception of valence.

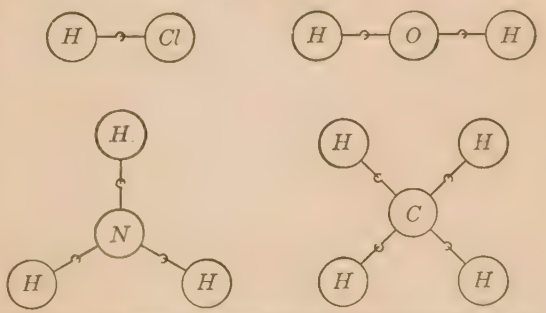


Fig. 67. Diagram representing the valence of atoms by bonds or hooks.

The accompanying diagrams (Fig. 67) represent such an imaginary linkage of the atoms in hydrogen chloride, water, ammonia, and marsh gas. It is obvious that if the elements unite with one atom of hydrogen, they must have only one bond, or hook; their valence is one. Similarly, elements which combine with two, three, and four atoms of hydrogen have two, three, and four bonds respectively. If an element like zinc, which has a valence of two, unites with chlorine, which has a valence of one, it will require two chlorine atoms to link up with the two bonds of a single zinc atom. The formula will, therefore, be $ZnCl_2$.

105. Valences of common elements and groups. We may indicate the valence of an element or a group of elements by writing slightly above and to the right of the symbol a small Roman numeral; thus, H^{I}, O^{II}, N^{III}, C^{IV}. *We take* ***hydrogen*** *as our standard of valence.*

VALENCES OF SOME COMMON ELEMENTS AND RADICALS *

(This table is for reference)

I. MONOVALENT	II. DIVALENT	III. TRIVALENT	IV. TETRAVALENT
Hydrogen . . H	Oxygen . . . . O	Aluminum . Al	Carbon C
Chlorine . . . Cl	Sulfur . . . . . S	Bismuth . . . Bi	Silicon . . . . . Si
Sodium . . . . Na	Zinc . . . . . Zn	Antimony . . Sb	Tin . . . . . Sn (ic)
Potassium . . K	Magnesium . Mg	Iron . . . . . Fe (ic)	Sulfur . . . . . S
Bromine . . . Br	Calcium . . . . Ca	Phosphorus . P	
Iodine I	Barium . . . . Ba	Nitrogen . . . N	
Fluorine . . . . F	Mercury . . . Hg (ic)	Phosphate . . PO_4	V. PENTAVALENT
Silver . . . . . Ag	Copper . . . . . Cu		
Mercury . . . Hg (ous)	Iron . . . . . Fe (ous)		Nitrogen . . . N
Ammonium . NH_4	Tin . . . . . Sn (ous)		Phosphorus . P
Hydroxide . . OH	Sulfate . . . . . SO_4		Antimony . . Sb
Nitrate . . . . . NO_3	Carbonate . . CO_3		

Using the above system for indicating the valence of an atom, we have shown in the table the valences of the common elements and of some common groups of elements. Certain groups of elements, like the hydroxyl (OH) group in bases, and the sulfate (SO_4) group in sulfuric acid, the nitrate (NO_3) group in nitric acid, and the ammonium (NH_4) group in ammonium compounds, remain intact throughout a number of reactions.

* It is not necessary at present to commit to memory this entire valence table.

Such groups of elements act very much like a single element and are called **radicals.** Radicals have valences just as do elements. Elements or groups which have the valence of one are called **monovalent;** if they have a valence of two, **divalent.**

106. Variable valence. It will be seen in the valence table that certain elements are indicated as having more than one valence. Such facts complicate the general rules of valence. Almost all elements form a certain number of compounds in which they have an unusual valence. For example, the valence of carbon is almost without exception four, as in carbon dioxide (CO_2) (oxygen is divalent, and there are two oxygen atoms). But in carbon monoxide (CO) the valence is two. Such exceptions are rare and must simply be learned as they occur. A few elements, like iron, form *two* series of compounds in which the element has different valences. For example, we have a number of compounds of iron called **ferrous** compounds, in which iron has a valence of **two;** others are called **ferric** compounds, in which iron has a valence of **three.** Such elements are said to have a variable valence.

107. Applications of valence. Let us now see how we can apply the information in the valence table to the writing of formulas. At this point we shall discuss only two cases:

1. When two elements (or radicals) which have the same valence unite to form a compound, they will combine atom for atom, as shown in the following examples. Note that valences are indicated by Roman numerals placed above each symbol.

Hydrogen chloride	$\overset{I}{H}\overset{I}{Cl}$	Iron sulfide	$\overset{II}{Fe}\ \overset{II}{S}$
Sodium chloride	$\overset{I}{Na}\overset{I}{Cl}$	Aluminum phosphate	$\overset{III}{Al}\ \overset{III}{PO_4}$
Copper oxide	$\overset{II}{Cu}\overset{II}{O}$	Silicon carbide	$\overset{IV}{Si}\ \overset{IV}{C}$

2. When two elements (or radicals) which have different valences unite to form a compound, they will combine so that *the total valences of one element equal the total valences of the other.*

For example, water is $\overset{\text{I}\ \ \text{II}}{H_2O}$. Since the valence of hydrogen is I and that of oxygen is II, we must take 2 atoms of hydrogen as indicated by the subscript 2 written after the H. Again, aluminum chloride is $\overset{\text{III}\ \text{I}}{AlCl_3}$ because aluminum has a valence of III and chlorine a valence of I. Carbon dioxide is $\overset{\text{IV}\ \ \text{II}}{C\ O_2}$. Because carbon has a valence of IV and oxygen II, we must have 2 atoms of oxygen for each atom of carbon. Aluminum oxide is $\overset{\text{III}\ \ \text{II}}{Al_2O_3}$. Since the valence of aluminum is III and of oxygen is II, and since the smallest number which is divisible by 3 and 2 is 6, we must have two atoms of aluminum to make its total valence six, and three atoms of oxygen, or Al_2O_3.

In writing formulas of molecules made up of two atoms or radicals of unequal valence we shall find the following RULE FOR VALENCE helpful:

Valence × *number of atoms* (or radicals) in the case of one element (or radical) *equals valence* × *number of atoms* (or radicals) in the case of the other.

108. How to learn the valence of the elements. It is very important to *learn the valence of each element or radical as we study it, and always to use it in writing formulas.* The student will find it good practice to check up every formula that he writes in order to make sure that the total valences of the two halves of the compound balance. Thus, if we write zinc nitrate $ZnNO_3$ and then mark the valences as follows: $Zn^{II}(NO_3)^{I}$, we see at once that the correct formula must be $Zn(NO_3)_2$. The chemist does not memorize the entire table of valences, but he remembers the formula of at least one simple compound of each element. For example, suppose he wishes the valence of mercury. Perhaps he recalls that the formula of the red oxide of mercury is HgO^{II}. Then, since the valence of oxygen is two, the valence of mercury in this compound is also two.

Exercises

1. Write the formulas for the following oxides:
   (*a*) calcium oxide
   (*b*) magnesium oxide
   (*c*) zinc oxide
   (*d*) mercuric oxide
   (*e*) silver oxide.
2. Write the formulas for the following hydroxides:
   (*a*) potassium hydroxide
   (*b*) ammonium hydroxide
   (*c*) calcium hydroxide
   (*d*) aluminum hydroxide
   (*e*) cupric hydroxide
3. Write the formulas for the following compounds:
   (*a*) zinc chloride
   (*b*) phosphoric pentoxide
   (*c*) copper sulfide
   (*d*) zinc sulfate
   (*e*) calcium carbonate
4. Mark the valences of the radicals in the following compounds:
   (*a*) Na_2SO_4
   (*b*) $KClO_3$
   (*c*) Ag_2CO_3
   (*d*) $PbCrO_4$
   (*e*) $Ca_3(PO_4)_2$
5. Mark the valences of the elements and radicals in the following compounds:
   (*a*) SiO_2 (sand)
   (*b*) CCl_4 (" carbona ")
   (*c*) $CuSO_4$ (blue stone)
   (*d*) MnO_2 (pyrolusite)
   (*e*) $HgCl_2$ (corrosive sublimate)

SUMMARY OF CHAPTER IX

THE CHEMICAL SYMBOL of an element represents one atom of the element; it also signifies the atomic weight of the element, usually in grams.

THE FORMULA of a compound shows what elements constitute the compound and also the composition by weight.

THE VALENCE of an atom is the number of hydrogen atoms with which it will combine or which it will replace. This may be represented by supposing that each atom has a certain number of hooks, or bonds, which enable it to join some other atom or atoms. This is merely a mechanical analogy.

A RADICAL is a group of elements that acts like a single element in a chemical reaction.

IN WRITING FORMULAS of binary compounds (two elements only) the total number of bonds of one element must equal the total number of bonds of the other element.

Questions

1. Mark the valences in the following formulas:

SO_3; CO; P_2O_5; $PtCl_4$; KI.

2. Correct the following formulas:

$ZnNO_3$; $CaCl_3$; $Cu(NO_3)_4$; $AgCl_2$; Al_3O_2.

3. Write the formulas of the following compounds and indicate the valence of each element or radical: (*a*) magnesium oxide, (*b*) aluminum chloride, (*c*) potassium nitrate, (*d*) silver sulfate, (*e*) ammonium chloride.

4. Write the names of the compounds listed in the first group (*a*) and write the formulas of those given in the second group (*b*):

(*a*) SnS_2; H_3PO_4; Tl_2O; $CrCl_3$; H_2S; $Ca(NO_3)_2$; $AlPO_4$.

(*b*) Tin chloride, thallium nitrate, chromium oxide, calcium phosphate, aluminum sulfide.

5. Given the valence of B as *two*, derive the probable valences of A, C, and D from the following formulas:

A_2B_3; B_2C; B_5D_2.

What would be the formula of a compound of A with C? of C with D?

CHAPTER X

CHEMICAL EQUATIONS

Uses of chemical equations — how to write equations — five steps — what an equation does not show — review equations of reactions studied.

Five types of reactions — reversible reactions.

109. Why chemical equations. The principal use which the chemist makes of symbols and formulas is in writing in a condensed and precise form a large amount of information about chemical changes, or reactions. Inasmuch as matter is indestructible (Law of Conservation of Matter), *we represent these changes, or reactions, as* ***equations.*** There is the same amount of each element after the change as before.

110. How to write equations. Chemical equations are based on experimental facts and represent chemical reactions, or changes, which actually occur. It is quite impossible to remember all the equations you will need. We shall endeavor in this chapter to show you *the mechanical features* about writing equations for those reactions which you have already studied. In this work it is well to remember that **a chemical equation is either all right or all wrong.**

The symbols and formulas of all the *materials undergoing change* are placed on the *left;* those of the new *products* resulting from the change, on the *right;* the *arrow* means *forms* or *gives.* For example, the union of iron and sulfur to form iron sulfide is expressed thus:

$$Fe + S \longrightarrow FeS$$

The burning of magnesium in oxygen might at first be expressed thus:

$$Mg + O_2 \longrightarrow MgO$$

But this equation is **wrong** because we have *two* atoms of oxygen on the left and *only one* atom on the right side; this would indicate that some of the oxygen had been lost. The very word "equation" means that there must be just as many atoms of each element after the change (on the right) as before (on the left). We can "balance" the equation, as it is called, thus:

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

In decomposing potassium chlorate by heat we might write the equation at first thus:

$$KClO_3 \longrightarrow KCl + O_2$$

and then balance it thus:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

From a study of the above it will be seen that these equations are not algebraic; they represent chemical changes which actually take place.

Before we can write an equation we must know:

(1) *that the change takes place;*
(2) *what substances are involved;*
(3) *what the products are; and*
(4) *the formulas of all the substances involved and of all products.*

111. Summary of the necessary steps. In making a chemical equation there are *five* steps:

(1) Write *on the left* the formula of each substance taking part in the reaction.

(2) Write *on the right* the formula of each substance known to be produced.

(3) Correct the right-hand side by increasing the number of molecules so as to use all the elements on the left.

(4) Correct the left-hand side by increasing the number of molecules needed by the substances produced.

(5) Check up to make sure that each atom of all the elements is accounted for.

For example, hydrogen burns in oxygen and produces water.

(1) $H_2 + O_2$

(2) $H_2 + O_2 \longrightarrow H_2O$

(3) $H_2 + O_2 \longrightarrow 2\,H_2O$

(4) $2\,H_2 + O_2 \longrightarrow 2\,H_2O$

(5) We have 4 atoms of hydrogen in the 2 molecules of hydrogen on the *left*, and we have 4 atoms of hydrogen in the 2 molecules of water on the *right*. We have 2 atoms of oxygen in 1 molecule of oxygen on the *left*, and we have 2 atoms of oxygen in the 2 molecules of water on the *right*.

112. Cautions. Use the **molecular formulas** for the gaseous elements. Thus, the molecular formulas of oxygen, hydrogen, nitrogen, and chlorine are O_2, H_2, N_2, Cl_2.

Remember that the number placed before a formula multiplies the *whole* formula. Thus, $2\,H_2O$ is the same as $2(H_2O)$, which means two molecules of water consisting of 4 atoms of hydrogen and 2 atoms of oxygen.

We balance equations *not* by altering the formulas of the substances, but by taking the proper number of molecules so that the number of atoms of each element is the same on both sides.

113. What an equation does not show. Chemical changes will usually occur only under certain *conditions*, which are not indicated in the equation.

For example, the equation

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

does not show that it is necessary to keep heating the red oxide of mercury in order to decompose it. The equation

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

does not indicate that the sulfuric acid must be diluted with water.

In general, the materials which are present but which undergo no change, such as water used as a solvent and the various catalysts, are not represented in the equation. Finally, we do

not as a rule try to show the amount of heat which is evolved in the chemical reaction. For example,

$$C + O_2 \longrightarrow CO_2$$

shows that carbon unites with oxygen to form carbon dioxide; but it does not tell us *how much heat is produced*, a piece of information which is most important for the industrial chemist.

114. Equations for reactions studied. We shall now write chemical equations for the reactions which we have studied up to this point, and which we have hitherto summarized by words. *The student will do well to master thoroughly all these equations.*

When water is electrolyzed it is decomposed into free hydrogen and oxygen. The equation for this is:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

We have to take two molecules of water in order to provide two oxygen atoms, since the formula for free oxygen is O_2.

When mercury oxide is heated, oxygen and mercury result. The equation is:

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

Again, we take two molecules of mercury oxide, so that we may have enough oxygen atoms to form a molecule. The mercury formed is a liquid; and we have reason to believe that the atoms in metals are often not united in molecules. Hence we represent them as in this case: 2 Hg *not* Hg_2, two single atoms of mercury. We also think a molecule of mercury is composed of one atom.

Five Types of Reactions

115. Simple decomposition. This type of chemical change involves only one substance, which breaks down by chemical change into two or more simpler substances. Such a reaction is called a **simple decomposition.** The decomposition of water into hydrogen and oxygen is an example of this type of chemi-

cal change. The decomposition by heat of mercuric oxide and potassium chlorate are also examples.

116. Direct combination or synthesis. Another type of chemical reaction, which is the *reverse* of simple decomposition, is **synthesis.** In this type we start with two or more substances and build up a compound. The following equations are the syntheses involving oxygen which we have thus far considered:

$$2\,Hg + O_2 \longrightarrow 2\,HgO$$
$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$
$$C + O_2 \longrightarrow CO_2$$
$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$
$$2\,C + O_2 \longrightarrow 2\,CO$$
$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

These equations represent the changes which took place when mercury, hydrogen, carbon, and phosphorus were heated in contact with pure oxygen or air. The last two equations show the burning of carbon in an insufficient supply of oxygen, producing carbon monoxide; and then the burning of carbon monoxide to carbon dioxide.

117. Simple replacement. The methods of preparing hydrogen (except the electrolysis of water) are examples of a type of chemical change called **replacement.** In this type of reaction one element takes the place of some other element or elements in a compound.

Thus, when zinc or magnesium acts on hydrochloric acid or sulfuric acid, the metal replaces the hydrogen:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2$$

When steam is passed over hot iron, the iron replaces the hydrogen of the water, forming the magnetic oxide of iron (Fe_3O_4):

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2$$

When metallic sodium or calcium is placed in water, the metal replaces the hydrogen of the water, forming sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$):

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$
$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$$

NOTE that in order to be able to represent the hydrogen in the molecular state (H_2) we must prefix the coefficient 2 in several places.

118. Replacement reactions. When one element of a compound replaces another, the number of atoms of the elements concerned must be such that the valences of the replacing element must equal the valences of the element replaced. Thus, when zinc replaces hydrogen in hydrochloric acid, each atom of zinc replaces two atoms of hydrogen, since the valence of zinc is two and the valence of hydrogen one:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

When aluminum reacts with hydrochloric acid, three atoms of hydrogen appear for every atom of aluminum, since the valence of the metal is three:

$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2$$

This use of the rules of valence will be found helpful in writing replacement reactions.

119. Double decomposition. Probably the commonest type of chemical reaction involves the interaction of two compounds to produce two other compound products. This is called **double decomposition** because each compound apparently breaks up into two parts, each of which unites with a different part of the other compound.

FOR EXAMPLE, take the reaction of hydrochloric acid (HCl) on marble ($CaCO_3$) to form calcium chloride ($CaCl_2$) and carbonic acid (H_2CO_3):

$$2\,HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3$$

The carbonic acid decomposes into water (H_2O) and carbon dioxide (CO_2):

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

120. Oxidation and reduction. The significance of oxidation and reduction has already been considered. We need now simply to write equations for some of the cases which we have met:

$$CuO + H_2 \longrightarrow Cu + H_2O \quad (\S\ 42)$$

$$CO_2 + C \longrightarrow 2\,CO \quad (\S\ 71)$$

121. Reversible reactions. When we dissolve carbon dioxide gas in water, there is a combination between the water and the carbon dioxide to form the compound carbonic acid:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

If we heat such a solution of carbonic acid, the carbon dioxide gas is driven off and we finally end with only water:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

This reaction is just the reverse of the first; whether the reaction goes one way or the other depends on the conditions, in this case primarily on the temperature. We call such a reaction a **reversible reaction** and indicate it by writing a double arrow; thus:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

This equation tells us that the reaction will proceed one way or the other according to slight changes in conditions.

SUMMARY OF CHAPTER X

AN EQUATION represents an actual chemical reaction. It is a picture of the molecular condition of a certain number of atoms before and after a chemical change.

A chemical equation must always be *balanced;* it must have the same number of atoms of each element on one side as on the other.

BEFORE WE CAN WRITE AN EQUATION WE MUST KNOW:

(1) that the change takes place;

(2) what substances are involved;

(3) what the products are;

(4) the formulas for all the substances involved and all the products.

A chemical equation *does not indicate* the conditions of the reaction. Catalysts and solvents, which are not affected, are not expressed. Usually the heat effects are not indicated.

CHEMICAL CHANGES MAY BE CLASSIFIED AS:

(a) simple decomposition
(b) direct combination
(c) simple replacement
(d) double decomposition
(e) oxidation and reduction

A REVERSIBLE REACTION is one in which the reaction may proceed in either direction according to slight changes in conditions.

Questions

1. Why is a chemical equation called an *equation?*

2. What is the difference between O_2 and 2 O?

3. What is the difference between simple decomposition and double decomposition?

4. When zinc and sulfur are heated together, zinc sulfide (ZnS) is formed. Write the equation.

5. When tin is heated in the air, tin oxide (SnO_2) is formed. Write the equation.

6. When aluminum reacts with hydrochloric acid (HCl), hydrogen and aluminum chloride ($AlCl_3$) are formed. Write the equation.

7. When iron is burned in oxygen, the product is the magnetic oxide of iron (Fe_3O_4). Write the equation.

8. When carbon dioxide is bubbled through limewater ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) and water are produced. Write the equation.

9. What important facts about a chemical reaction are not expressed in a chemical equation?

10. Balance the equation in each case:

$$O_2 \longrightarrow O_3$$
$$Na + O_2 \longrightarrow Na_2O_2$$
$$P + Cl_2 \longrightarrow PCl_5$$
$$Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$$
$$H_2S + AsCl_3 \longrightarrow HCl + As_2S_3$$

11. Write the name of each substance under the formulas used in the equations just given.

12. Write the reversible equation for the classic experiment of Lavoisier with mercury and air.

Review Questions

1. State the Law of Multiple Proportions. Illustrate its meaning by examples.

2. How would you distinguish in the laboratory between hydrogen and carbon monoxide?

3. Describe a laboratory method, involving a chemical change, by which you could distinguish between nitrogen and carbon dioxide.

4. Write equations for the following reactions, using formulas throughout. (The equation must be absolutely correct to receive credit.)

(*a*) zinc and sulfuric acid (dilute)
(*b*) cupric oxide and hydrogen
(*c*) calcium hydroxide and carbon dioxide
(*d*) iron and hydrochloric acid
(*e*) phosphorus and oxygen

5. Put into words all the information which is conveyed by the equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

CHAPTER XI

CHEMICAL COMPUTATIONS

Importance of computations — quantitative meaning of equations — problems involving weight only — significant figures — problems involving weight and volume — general rules.

122. Importance of chemical computations. To the industrial chemist (Fig. 68) the chemical equation is very important because it enables him to *calculate* just how much material he

Courtesy of *The B. F. Goodrich Rubber Co.*

Fig. 68. Weighing out the materials to make rubber.

ought to use in a given reaction and how large an amount of product he may hope to get. In actual practice, however, he very seldom gets the full amount of the product as calculated

from the equation, and therefore he computes the efficiency of his process. These computations are all based on the chemical equations of the reactions, and require only the simplest arithmetical work.

123. Percentage composition from the formula. If we know the formula of a compound and have a table of atomic weights, we can easily compute the percentage of each element in the compound. Given the formula of potassium chlorate as $KClO_3$, and the atomic weight of potassium 39, of chlorine 35.5, and of oxygen 16. Then the formula represents

39.0 parts by weight of potassium
35.5 parts by weight of chlorine
3×16 or 48.0 parts by weight of oxygen
or 122.5 parts by weight of potassium chlorate.

Therefore potassium chlorate contains

$$\frac{39}{122.5} = 0.318 \text{ or } 31.8 \text{ per cent of potassium,}$$

$$\frac{35.5}{122.5} = 0.290 \text{ or } 29.0 \text{ per cent of chlorine, and}$$

$$\frac{48}{122.5} = 0.392 \text{ or } 39.2 \text{ per cent of oxygen.}$$

Problems

1. Calculate the percentage composition of the following compounds:

(*a*) common salt ($NaCl$)
(*b*) saltpeter (KNO_3)
(*c*) black copper oxide (CuO)
(*d*) carbon dioxide (CO_2)
(*e*) mercuric oxide (HgO)
(*f*) iron oxide (Fe_3O_4)
(*g*) marble ($CaCO_3$)
(*h*) sulfuric acid (H_2SO_4)
(*i*) zinc sulfate ($ZnSO_4$)
(*j*) cane sugar ($C_{12}H_{22}O_{11}$)

Hint. Use Table of Approximate Atomic Weights on back cover.

2. The formula for crystallized barium chloride is $BaCl_2 \cdot 2\,H_2O$, which indicates that there are two molecules of water united with each molecule of the anhydrous barium chloride. Calculate the percentage of water of crystallization in crystallized barium chloride.

3. The formula for alum is $KAl(SO_4)_2 \cdot 12\ H_2O$. Compute the percentage of water of crystallization in alum.

4. If 10 grams of crystallized sodium carbonate (sal soda) are carefully heated, the dehydrated sodium carbonate (Na_2CO_3) which is left weighs only 3.70 grams. Compute the number of molecules of water of crystallization.

5. In one ton (2000 lb.) of Glauber's salt ($Na_2SO_4 \cdot 10\ H_2O$), how much (pounds) is water of crystallization?

124. Quantitative meaning of equations. An equation when properly balanced tells us what substances react and what the products are; it also gives us the number of molecules of each substance involved; finally, *by using the atomic weights, we learn the relative weights of the different substances in the equation.*

For example, in the equation for preparing oxygen by heating potassium chlorate we may compute the relative weights of potassium chlorate, potassium chloride, and oxygen thus:

$$\underset{(2 \times 122.5)}{2\ KClO_3} \longrightarrow \underset{(2 \times 74.5)}{2\ KCl} + \underset{(3 \times 32)}{3\ O_2}$$
$$\underset{245}{} \qquad \underset{149}{} \qquad \underset{96}{}$$

The weight of each molecule (**formula weight**) may be found by adding the atomic weights of the elements involved:

formula wt. of $KClO_3 = 39 + 35.5 + (3 \times 16) = 122.5$
formula wt. of $KCl = 39 + 35.5 = 74.5$
formula wt. of $O_2 = 2 \times 16 = 32$

Since there are two molecules of potassium chlorate and of potassium chloride in the equation, we multiply their formula weights by two; and as there are three molecules of oxygen, we multiply its formula weight by three.

We can now read this equation as follows: *245 parts by weight of potassium chlorate give 149 parts by weight of potassium chloride and 96 parts by weight of oxygen.*

125. Problems involving weight only. What weight of sulfur will be just enough to unite with 10 grams of iron to form iron sulfide (FeS)?

To avoid mistakes it is well to arrange the work very clearly and to do it methodically.

We *first* write the equation:

$$Fe + S \longrightarrow FeS$$

Then we write under each symbol and formula the weight it represents (using the approximate atomic weights given on the back cover):

$$\begin{array}{ccccc} Fe & + & S & \longrightarrow & FeS \\ 56 & & 32 & & 88 \end{array}$$

This means that 56 parts by weight of iron combine with 32 parts by weight of sulfur to give 88 parts by weight of iron sulfide. *We have here the quantitative meaning of the equation.*

Next, we again read the problem and place above the symbol for iron the actual weight given, which is 10 g., and above the formula for sulfur an x, which is the weight we wish to find; thus:

$$\begin{array}{ccccc} 10\text{ g.} & & x\text{ g.} & & \\ Fe & + & S & \longrightarrow & FeS \\ 56 & & 32 & & 88 \end{array}$$

Finally, we state the fractional equation thus:

$$\frac{10}{56} = \frac{x}{32}$$

Hence $$x = \frac{32 \times 10}{56}$$ or **5.71 grams,** wt. of sulfur.

Now we shall **check up** the reasonableness of our answer by roughly estimating what it ought to be. In this case we know that 56 parts of iron will need 32 parts of sulfur. Therefore we shall need about four-sevenths as much sulfur as the iron with which we started. Hence our answer 5.71 is reasonable. In this way we may quickly detect such a mistake as the misplacing of a decimal point or the inverting of a fraction.

126. Another example. Suppose we want to compute what weight of iron sulfide (FeS) can be made from 10 grams of iron, assuming that the necessary sulfur is available.

$$\begin{array}{ccccc} 10\text{ g.} & & & & x\text{ g.} \\ Fe & + & S & \longrightarrow & FeS \\ 56 & & & & 88 \end{array}$$

$$\frac{10}{56} = \frac{x}{88}$$

$$x = \frac{88 \times 10}{56} = \textbf{15.7 grams,} \text{ wt. of iron sulfide.}$$

CHECK: Wt. of iron (10 g.) + wt. of sulfur (5.71 g.) = wt. of iron sulfide (15.7 g.)

127. Significant figures. The atomic weights which are to be used in calculating such problems are the **approximate values** given in the table on the back cover. These are not the most accurate values which have been determined, but they are close enough for practical purposes. It is only in very accurate chemical work that we use the most precise values that have been obtained. It will be seen that these numbers have not more than *three figures* in them; the fourth, fifth, or sixth figure counting from the left has been rounded off. For example, the precise atomic weight of barium is 137.37. We call this 137. In the same way, in carrying out arithmetical processes *we should express the answer in the nearest* ***three*** *figures*. Since we have used atomic weights that have not more than three figures in them, the fourth, fifth, and sixth figures in a possible answer will have no significance. We therefore say that the problems in this book should be carried to but *three significant figures*. Zeros which occur before a set of numbers, as for example in 0.00672, are not considered as significant figures; the three significant figures here are 6, 7, and 2.

128. General rules for solving weight problems.

(1) Write the complete equation for the reaction in question.

(2) Write the actual weight which is given above the formula of the substance and x above the formula of the substance the weight of which is wanted.

(3) Write under the formula of each substance involved in the problem its formula weight for which each complete formula stands.

(4) Make an equation of two fractions, one of which is the actual weight over the formula weight of the substance given and the other of which has the x over the formula weight of the substance required. *The actual weights are the numerators and the formula weights the denominators.*

(5) Solve this equation and decide whether the answer is reasonable by making a rough calculation as to what the answer should be.

129. An illustrative problem. How many grams of potassium chlorate are necessary to prepare 10 grams of oxygen?

Let us proceed according to our five general rules:

(1) The complete equation

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

(2) Write in the actual weights

$$\begin{array}{r} x\text{ g.} \qquad\qquad 10\text{ g.} \\ 2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2 \end{array}$$

(3) Underneath write the formula weights

$$\begin{array}{r} x\text{ g.} \qquad\qquad 10\text{ g.} \\ 2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2 \\ 2(122.5) \qquad\qquad 3(32) \\ 245 \qquad\qquad 96 \end{array}$$

(4) Make the fractional equation

$$\frac{x}{245} = \frac{10}{96}$$

(5) Solve $\quad 96\,x = 10 \times 245$

$$x = \frac{10 \times 245}{96} = \textbf{25.5 grams.}\quad \text{Answer.}$$

CHECK. Since 245 is about $2\frac{1}{2}$ times 96, we should expect the answer to be about 25 g.

SUMMARY OF CHAPTER XI

A CHEMICAL FORMULA represents the weights of the elements which the compound contains.

A CHEMICAL EQUATION represents the *relative weights* of all of the substances involved. By *writing* out equations and then by using atomic and formula weights, it is possible to calculate how much of any substance may be required or produced in a chemical change.

THE ACTUAL WEIGHT of one substance in a chemical equation is the same fractional part of its formula weight as the actual weight of any other substance in the same equation is of its formula weight. Such calculations deal with *but two* of the substances at a time.

Problems

1. How much potassium chlorate must be used to generate 2 grams of oxygen?

2. How much mercuric oxide must be used to generate 2 grams of oxygen?

3. How many grams of mercury would result from the complete decomposition of 5 grams of mercuric oxide?

4. How many grams of zinc would be needed to produce 8 grams of hydrogen (*a*) if hydrochloric acid were used? (*b*) If sulfuric acid?

5. How many grams of hydrogen will be produced by passing steam over 100 grams of iron until all the iron is converted into the magnetic oxide of iron (Fe_3O_4)?

6. Ten grams of copper oxide (CuO) are reduced to metallic copper by heating in a stream of dry hydrogen. Compute (*a*) the weight of water formed and (*b*) the weight of hydrogen required.

7. (*a*) Compute the weight of oxygen formed by heating 100 grams of sodium chlorate ($NaClO_3$). (*b*) By heating the same weight of potassium chlorate ($KClO_3$). (*c*) Which is the cheaper source of oxygen when sodium chlorate costs 15 cents per kilogram and potassium chlorate 20 cents per kilogram?

8. If concentrated hydrochloric acid contains only 35 per cent of pure hydrogen chloride, how many grams of hydrogen can be generated

by using 100 cc. of the acid (density 1.2 g. per cc.) with an excess of zinc?

9. If coal contains 85 per cent of carbon, (*a*) how many pounds of carbon dioxide will be produced when a ton (2000 lb.) of coal is burned? (*b*) How many tons of air will be required, if we assume that about 23 per cent of the air by weight is oxygen?

10. If a chemist uses 10.5 grams of sulfuric acid and 6.5 grams of zinc in his hydrogen generator, (*a*) which of these two substances will be left? (*b*) How much of it?

Topic for Further Study

Practical chemical calculations. Suppose hydrogen is desired for balloons. How much would the raw materials cost for making 100,000 cu. ft. of the gas from (*a*) zinc and acid; (*b*) iron and acid? What would be the cheapest acid to employ? Which of these methods would seem to be the more economical? There are other important items of expense beside raw materials; a final answer to the cost of manufacturing hydrogen could be given only if these other expenses were known. What methods were used to prepare hydrogen for the balloons used in the World War? (Market prices of materials will be found in trade journals, such as *Chemical and Metallurgical Engineering*.)

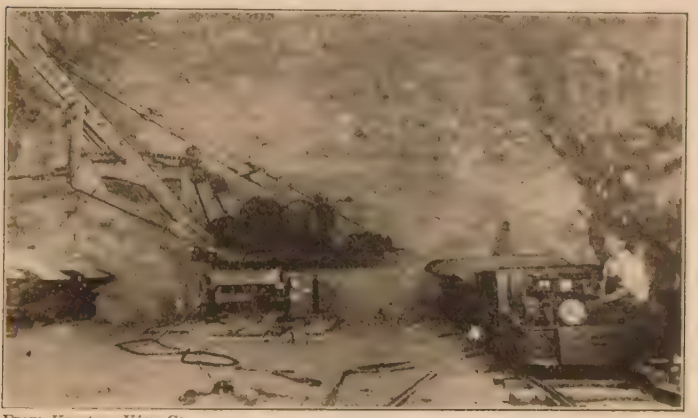
CHAPTER XII

COMMON SALT, CHLORINE, AND HYDROGEN CHLORIDE

Importance of salt — sodium chloride — electrolysis of brine — chlorine, preparation and properties, — common salt and sulfuric acid — laboratory and commercial preparation of hydrogen chloride — properties — hydrochloric acid — uses of hydrochloric acid — composition of hydrogen chloride by electrolysis and by synthesis.

130. Importance of common salt. Thus far we have been principally concerned with water and its constituent elements, and with the air and its components. Another very familiar substance is common salt. This salt we shall show is made up of the two elements sodium (a metal) and chlorine (a gas) and so is called sodium chloride (NaCl). Large amounts of it are used in the household in the preparation of our food; in fact, the quantity of salt usually employed in flavoring foods is far greater than can be utilized in the body. The coarse salt found in nature, known as rock salt, is used for freezing ice cream, feeding cattle, curing meat, and preserving fish. But the biggest market for salt is in the chemical industries. Since it is the cheapest compound of *chlorine*, we shall see how it is used to prepare chlorine gas, hydrochloric acid, bleaching powder, and many other chlorine compounds. Salt is also the cheapest *sodium* compound, and we shall presently see how it is used as the raw material for the manufacture of washing soda, caustic soda, baking ash, and many other sodium compounds. Among the other industries which use large quantities of salt, the manufacture of pottery, glass, and soap should be included.

131. Common salt, or sodium chloride (NaCl). This substance occurs as rock salt in large beds (Fig. 69) which are found mainly in the United States, Austria, and Germany. In this country Michigan is the largest producer, but New York state furnishes a purer grade of salt. The United States produces more salt than any other nation. It also forms the major part of the dissolved material in sea water and in certain inland lakes,



From *Keystone View Co.*

Fig. 69. Mining salt in Louisiana with the aid of electrical machinery.

like Great Salt Lake and the Dead Sea. Salt for commercial purposes is obtained by mining rock salt and by the evaporation of sea water or the brine which is obtained from salt wells located near salt deposits. In certain places, such as on some of the shores of San Francisco Bay (Fig. 70), the sea water is run into shallow basins and is evaporated by the heat of the sun. In other places, as in Russia, the water is frozen out of the solution. But usually the solution is evaporated by heat under reduced pressure. The pure salt crystallizes out first and, if necessary, can be collected and recrystallized for further purification.

When it is to be used for industrial purposes, it is generally sold in the form of **rock salt,** which is made by crushing to a

uniform size the lumps as mined. For cooking purposes and for the table it is sold as a fine crystalline powder. It is generally contaminated with a small quantity of calcium and magnesium chlorides, which readily absorb moisture from the air and cause the salt to stick together in lumps. Chemically pure salt, from which these impurities have been removed, does not absorb water from the air.

Fig. 70. Gathering salt from San Francisco Bay with the aid of a tractor.

132. Electrolysis of salt solution. When an electric current passes through a concentrated solution of sodium chloride, chlorine gas is evolved at the anode (positive terminal) and hydrogen at the cathode (negative terminal) (Fig. 71). Probably sodium is at first liberated at the cathode; but, as we have seen (§ 36), this element rapidly reacts with water, with the result that hydrogen is evolved and a substance called sodium hydroxide is left in solution. These changes can be represented by the following equations:

$$\underset{\text{sodium chloride}}{2\,NaCl} \longrightarrow \underset{\text{sodium}}{2\,Na} + \underset{\text{chlorine}}{Cl_2} \qquad \text{(electrolysis)}$$

$$\underset{\text{sodium}}{2\,Na} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{hydrogen}}{H_2}$$

This electrolytic method is one of the commercial methods of making chlorine. Industrial chlorine is usually very pure and is either used directly or is compressed and liquefied for transportation.

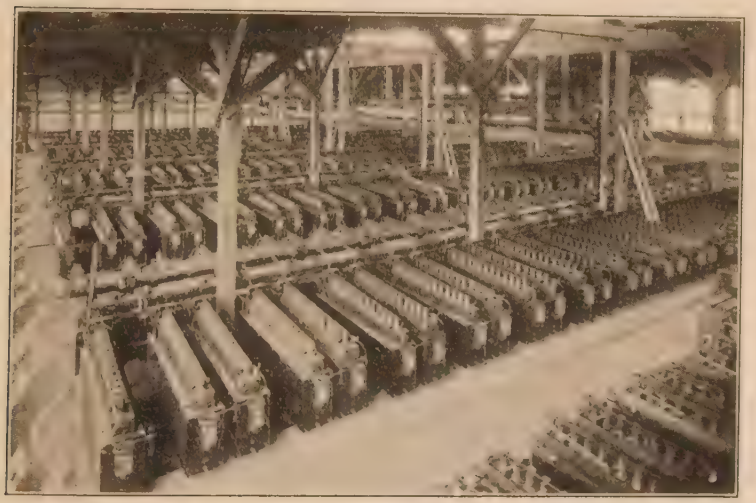


Fig. 71. Room containing several hundred cells each of which is decomposing brine into caustic soda, chlorine, and hydrogen.

133. Laboratory preparation of chlorine. In the laboratory chlorine is prepared from concentrated hydrochloric acid. This acid is treated with an oxidizing agent which oxidizes the hydrogen of the acid to water and sets chlorine free. Manganese dioxide (MnO_2) is commonly employed as the oxidizing agent. In this case the manganese unites with half the chlorine of the hydrochloric acid; the rest of the chlorine is evolved as a gas when the mixture is warmed. The reaction is as follows:

$$\underset{\text{hydrochloric acid}}{4\,HCl} + \underset{\text{manganese dioxide}}{MnO_2} \longrightarrow \underset{\text{manganese chloride}}{MnCl_2} + \underset{\text{water}}{2\,H_2O} + \underset{\text{chlorine}}{Cl_2\uparrow}$$

It will be noted that one of the products is a gas, chlorine. This is indicated by the arrow pointing *up*.

Instead of employing hydrochloric acid it is possible to use a mixture of sodium chloride and sulfuric acid, which produces hydrochloric acid. Since chlorine is moderately soluble in water, the gas is collected by the displacement of air, as shown in figure 72.

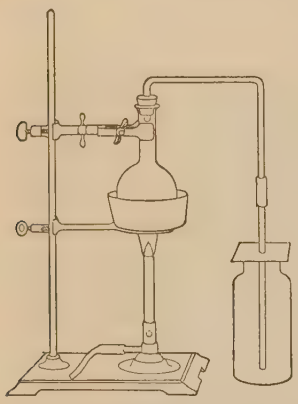


Fig. 72. Laboratory preparation of chlorine.

134. Properties. Chlorine is a greenish yellow gas with a very irritating odor. It is extremely poisonous and exposure even for short periods to a low concentration of it will produce serious lung trouble. For this reason it was the first "poison gas" used in the World War. A so-called "cloud attack" with this gas is shown in figure 73. It is about two and a half times as heavy as air. It can very readily be liquefied at ordinary temperatures by applying a pressure of between six and seven atmospheres. Liquid chlorine is now an article of commerce and is sold in strong steel cylinders.

135. Chemical activity. Chlorine is an extraordinarily active substance. It combines with a number of elements at room temperature, forming the chlorides with the evolution of much heat. Freshly powdered antimony (cold) and arsenic burst into flame when they are introduced into the gas. A jet of hydrogen if lighted in the air will continue to burn in an atmosphere of chlorine (Fig. 74). This combustion is unusual inasmuch as no oxygen is involved. The reaction which takes place and which produces heat and light is the combination of hydrogen and chlorine to form hydrogen chloride. The white fumes of hydrochloric acid can be seen if one breathes into the jar. Many compounds of carbon and hydrogen — for example, turpentine — react so vigorously with chlorine that a flame is

produced. The other products of the reaction are free carbon and hydrochloric acid.

Fig. 73. Cloud attack with chlorine during the World War. What one sees is the condensed moisture.

136. Chlorine water. Chlorine is somewhat soluble in water: one volume of water under ordinary conditions dissolves about three volumes of the gas. The chlorine is partly in true solution and partly present as two compounds, hydrochloric acid and hypochlorous acid (HOCl). This latter substance is unstable and breaks down easily, setting free oxygen. Industrially it is a very valuable substance because of its oxidizing power.

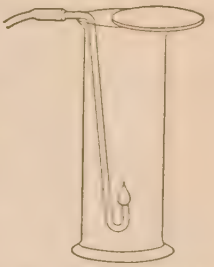


Fig. 74. Burning hydrogen in chlorine.

137. Uses of chlorine. This gas is very extensively used in the industries (see Industrial Chart on page 181). It enters into the manufacture of certain other chlorine

compounds, such as sulfur chloride, carbon tetrachloride, and chloroform. Its main use lies in the production of dilute solutions of hypochlorous acid or the salts of this acid, both of which are important as bleaching and disinfecting agents (Chapter XXV).

138. Action of sulfuric acid on common salt. We have already worked with **sulfuric acid** (H_2SO_4), a chemical which is doubtless the most important substance that the chemist uses. Let us find out what happens when this acid is added to common salt.

We place a pinch of sodium chloride in a test tube and add a few drops of concentrated sulfuric acid. If necessary we warm it slightly in order to start the action. We soon see bubbles of gas forming on the salt and rising through the acid, and we smell a sharp, choking odor. The gas itself has no color, but when we blow over the top of the tube, a white cloud is formed. A piece of moist blue litmus paper *turns from blue to red* when we bring it near the mouth of the tube. If we bring near the open end of the tube a piece of filter paper wet with ammonia water, a very dense white smoke appears. These are the characteristics of a gas known as **hydrogen chloride** (HCl).

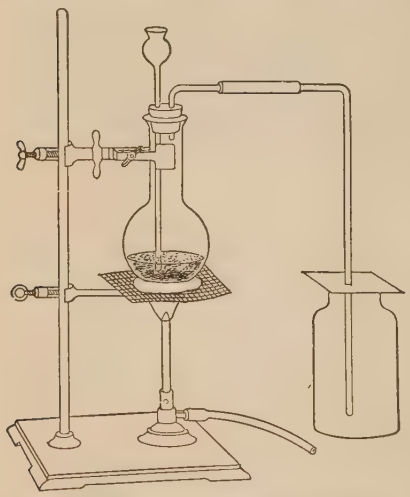


Fig. 75. Hydrogen chloride generator.

139. Preparation of hydrogen chloride. In order to study further the properties of hydrogen chloride, we may set up the apparatus shown in figure 75. The flask contains a handful of common salt. The sulfuric acid is introduced through a thistle tube which reaches nearly to the bottom of the flask. Since the gas (HCl) is extremely soluble in water, we cannot collect it over water. It is, however, heavier than air; so we may collect it in an

open bottle by *downward displacement* of the air. Heat must be applied *very gently* when it is necessary. The presence of the gas in the bottle is recognized by the pungent odor and by the white fumes which appear when the breath is blown over the top of the bottle.

The method used in manufacturing hydrogen chloride on a commercial scale is not different in principle from that just described. When sulfuric acid (H_2SO_4) and sodium chloride (NaCl) react, the hydrogen of the acid combines with the chlorine of the salt to form the gas hydrogen chloride (HCl), which is given off. There is left behind in the retort a white solid which is called sodium sulfate (Na_2SO_4). This reaction can be expressed thus:

$$\underset{\text{sulfuric acid}}{H_2SO_4} + 2\,\underset{\text{sodium chloride}}{NaCl} \longrightarrow \underset{\text{sodium sulfate}}{Na_2SO_4} + 2\,\underset{\text{hydrogen chloride}}{HCl}\uparrow$$

It will be noted that this is an example of **double decomposition** and that one of the products is a gas. Sulfuric acid is used because it boils at a comparatively high temperature (338° C.), while hydrogen chloride is a gas at room temperatures. If an excess of sulfuric acid is employed as in the laboratory experiment, sodium hydrogen sulfate ($NaHSO_4$) is left in the flask.

140. An experiment with hydrogen chloride. The extreme solubility of this gas in water may be strikingly shown in the following experiment:

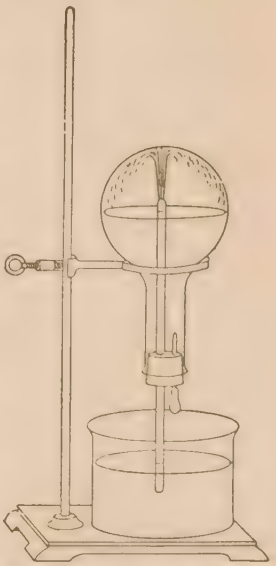


Fig. 76. Hydrogen chloride is extremely soluble in water.

We fill a dry flask with the gas and insert in it a two-hole rubber stopper, in one hole of which is a "dropper" containing water and in the other a straight glass tube drawn down to a small opening on the inside end. The apparatus is set up as shown in figure 76. Next we pinch the rubber bulb, expelling a few drops of water into the flask. This water dissolves so much of the gas that the water in the jar is forced by atmospheric pressure to behave like a fountain.

It is this great solubility of hydrogen chloride in water which causes the characteristic fuming of the gas in moist air. The moisture of the air dissolves the gas and then forms small droplets of the solution, which remain suspended in the air like white fog.

141. Properties. Hydrogen chloride is a colorless gas, about one-fourth heavier than air. It has a very irritating, sharp odor and is extremely soluble in water: one cubic centimeter of water dissolves between 400 and 500 cubic centimeters of the gas. Hydrogen chloride will not burn and will not support combustion. The dry gas reacts only very slowly with most metals at room temperature. It will react with some at a high temperature. The hydrogen of the compound is liberated as hydrogen gas, and the chlorine combines with the metal (simple replacement).

It reacts with zinc and the product is zinc chloride ($ZnCl_2$), a white solid. The equation for the reaction is:

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{hydrogen}\\\text{chloride}}}{2\,HCl} \longrightarrow \underset{\substack{\text{zinc}\\\text{chloride}}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

The above reaction is exactly analogous to that between steam and iron to give hydrogen and iron oxide. The equation for this reaction is:

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{steam}}{4\,H_2O} \longrightarrow \underset{\substack{\text{iron}\\\text{oxide}}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2\uparrow}$$

142. Hydrochloric acid. The solution of hydrogen chloride in water is known as **hydrochloric acid.** Its properties are quite different from those of the dry gas, and the two substances should not be confused. Solutions of the gas in water containing as much as 40 per cent by weight of the gas can be prepared. A solution containing more than 30 per cent of the gas is called **concentrated hydrochloric acid.** This is the concentration of the commercial acid which is known as "muriatic acid." When it is diluted with 3 or 4 times its volume

of water, we have **dilute** hydrochloric acid. A concentrated solution of the pure gas in distilled water is " chemically pure " (C. P.) hydrochloric acid. This is a colorless liquid with a density of about 1.2 grams per cubic centimeter.

Hydrochloric acid is a very active substance. We have already used it for preparing carbon dioxide (§ 64). It reacts vigorously with zinc, producing hydrogen. In fact, with all the common metals except mercury, silver, copper, and lead, hydrochloric acid produces hydrogen. The equation for the reaction with zinc is:

$$\underset{\text{zinc}}{Zn} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{2\,HCl} \longrightarrow \underset{\substack{\text{zinc}\\\text{chloride}}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

This reaction is exactly the same as that of the dry hydrogen chloride except that it takes place very rapidly and at room temperature.

143. Uses of hydrochloric acid. Very small quantities of hydrochloric acid are always found in the stomach, for its presence is necessary in the digestive process. This acid is produced in the body from the salt that is taken with the food.

Concentrated hydrochloric acid is manufactured in considerable quantities for use in the industries and in laboratories. It is generally shipped in large glass carboys (Fig. 77) packed in wooden boxes. It is used by tinmen and plumbers for cleaning metal surfaces which are to be soldered.

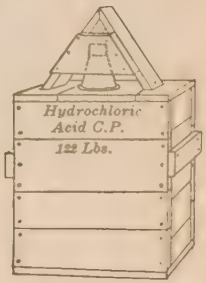


Fig. 77. Carboy of acid packed for transportation.

144. Chlorides. The compound resulting from the union of an element and chlorine is called a **chloride.** All the salts which are formed from hydrochloric acid are called chlorides, irrespective of the base employed. Whenever a metal, such as zinc, reacts with hydrochloric acid, the metallic chloride (as zinc chloride) is made. Sometimes a chloride is formed by the direct combi-

nation of an element and chlorine, as, for instance, antimony and chlorine (§ 135).

All the common chlorides are readily soluble in water except those of ***silver*** *(AgCl),* ***lead*** *($PbCl_2$), and* ***mercury*** *(HgCl).*

145. Test for a chloride. A solution of silver nitrate ($AgNO_3$) — which is made from silver and nitric acid — is a **test for a chloride,** because it produces a white, curdy precipitate (AgCl) with every solution which contains a chloride. A **precipitate** is an insoluble solid which results from a chemical action in solution.

Fig. 78. Pouring silver nitrate into sodium chloride precipitates silver chloride.

If we dissolve a pinch of sodium chloride (NaCl) in water and add a few drops of silver nitrate solution, a white, curdy precipitate (Fig. 78) consisting of silver chloride is at once produced. We may divide the liquid containing the precipitate into two parts and add ammonia water to one and nitric acid to the other. It will be seen that the precipitate dissolves in ammonia water and does not dissolve in nitric acid. It will also be observed that the *white precipitate turns purple on standing in the sunlight.*

The equation for this double decomposition is:

$$\underset{\text{sodium chloride}}{NaCl} + \underset{\text{silver nitrate}}{AgNO_3} \longrightarrow \underset{\text{silver chloride}}{AgCl}\downarrow + \underset{\text{sodium nitrate}}{NaNO_3}$$

NOTE. The small arrow after AgCl pointing *downward* indicates that the silver chloride is precipitated and drops *down.*

This test is a very sensitive one, and the presence of a very minute quantity of chloride can thus be recognized.

146. Analysis of hydrogen chloride. The fact that hydrogen chloride is composed of hydrogen and chlorine may be demonstrated in the same way that the composition of water is shown; that is, by electrolysis.

If concentrated hydrochloric acid is placed in the apparatus (Fig. 79) and an electric current is passed through the solution, we find that hydrogen is produced at the negative (−) carbon electrode and chlorine at the positive (+) carbon. At first the gases collect at unequal rates because the chlorine dissolves in the solution; but after a time the liquid becomes saturated, and both gases, the hydrogen and the chlorine, collect in the tubes in equal volumes.

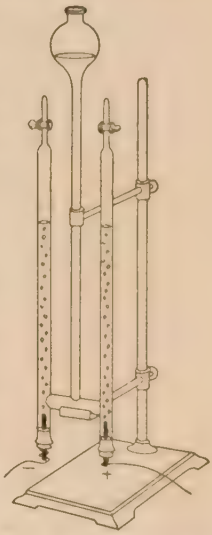


Fig. 79. Electrolysis of hydrochloric acid.

In this experiment we obtain from the aqueous solution of hydrogen chloride equal volumes of hydrogen and of chlorine.

147. Synthesis of hydrogen chloride. We may also, as in the case of water, reverse the experiment and *show the formation of hydrogen chloride by the synthesis of equal volumes of hydrogen and chlorine.*

A small bottle is filled with concentrated hydrochloric acid nearly up to the neck, and an electric current is sent through the solution for about 15 minutes. We then connect the exit tube with a stout glass tube (Fig. 80) which has a stopcock at each end. We allow the gases, hydrogen and chlorine, to pass through the straight tube and then to bubble through a sodium hydroxide solution. The whole apparatus has been covered with a dark cloth to prevent a premature explosion due to the sunlight. It is best to let the gases pass through the apparatus for at least 15 minutes more, then to close both cocks and to stop the current.

Fig. 80. Tube for synthesis of hydrogen chloride.

The mixture of hydrogen and chlorine may be exploded by an electric spark if the tube is provided with platinum wires; or it may be exploded still more easily by exposure to direct sunlight or to a magnesium flashlight. CAUTION! The gases explode instantly, but there is no noise, only a little click with a flash of light in the tube.

To show the volume of hydrogen chloride gas formed, we may place one end of the tube under some mercury in a dish and open the stopcock at that end. Since the mercury does not rise in the tube and no bubbles of gas escape, *the volume of the hydrogen chloride is just equal to the sum of the volumes of hydrogen and chlorine.*

If we now open one end of the tube beneath water, we notice that the water is sucked up into the tube with a rush. On testing the water in the tube we find that it is hydrochloric acid.

These experiments show that *one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride gas.*

$$\boxed{H_2} + \boxed{Cl_2} \longrightarrow \boxed{HCl}\boxed{HCl}$$

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vol. hydrogen chloride

This is a very interesting illustration of Gay-Lussac's Law of Volumes (§ 54).

SUMMARY OF CHAPTER XII

SODIUM CHLORIDE occurs abundantly in nature and is used in the preparation of other sodium and chlorine compounds.

CHLORINE is prepared industrially by the electrolysis of sodium chloride. It is prepared in the laboratory by the oxidation of hydrochloric acid with manganese dioxide.

PROPERTIES: Chlorine is a greenish yellow, poisonous gas with pungent odor. It is a very active element and combines with many elements at room temperature. It is somewhat soluble in water, and its water solution contains hypochlorous acid, which is an oxidizing agent.

USES. Chlorine is used for preparing solutions of hypochlorous acid and of its salts. The salts are used extensively in the industries.

HYDROGEN CHLORIDE IS PREPARED by the action of concentrated sulfuric acid on sodium chloride.

PROPERTIES: Hydrogen chloride is a colorless gas with a pungent odor. It forms a cloud with moist air, is extremely soluble in water, and is one-fourth heavier than air. The dry gas is inactive.

HYDROCHLORIC ACID (or muriatic acid) is a water solution of hydrogen chloride. It reacts with metals, such as zinc, evolving hydrogen.

COMPOSITION OF HYDROGEN CHLORIDE: one volume of hydrogen will combine with one volume of chlorine to yield two volumes of hydrogen chloride.

Questions and Problems

1. In the laboratory preparation of chlorine what is the purpose for which each of the two substances is used?

2. When salt, sulfuric acid, and manganese dioxide are used to prepare chlorine, what is the purpose of each?

3. Why is the commercial method of making chlorine not used in the laboratory?

4. Compare the densities of: (*a*) oxygen and chlorine; (*b*) hydrogen and hydrogen chloride; (*c*) chlorine and hydrogen chloride.

5. Write equations for the union of chlorine with: (*a*) sodium; (*b*) copper; (*c*) antimony; (*d*) iron; (*e*) phosphorus.

6. When a cylinder of hydrogen is placed above one containing chlorine, the two gases will mix slowly and after a time become a uniform mixture. Explain this fact.

7. How many grams of chlorine can be made from 348 grams of manganese dioxide and an excess of hydrochloric acid?

8. During the World War the United States government was making 100 tons of chlorine every 24 hours at the Edgewood Arsenal, Maryland. How many tons of pure salt were used every 24 hours? Assume that the electrolysis was 100 per cent efficient.

9. In preparing hydrogen chloride, what substance furnishes the hydrogen? What substance the chlorine?

10. Why is the aqueous solution of hydrogen chloride more useful than the dry gas?

11. Why does an open bottle of concentrated hydrochloric acid fume in the air and fume more strongly if the breath is blown across its mouth?

12. If you heat concentrated hydrochloric acid, what passes off? Give your reasons.

13. Metallic copper and hydrochloric acid do not react, but copper oxide (CuO) does dissolve readily in the acid. Write the equation.

14. Find the number of grams of hydrogen chloride generated by the complete reaction of 64 grams of sulfuric acid on an excess of sodium chloride.

15. Why does a tinman use muriatic acid in soldering metals?

16. Why is hydrochloric acid not shipped in tin cans?

17. What are the experimental difficulties in connection with the electrolysis of hydrochloric acid?

18. What precautions must be taken in the synthesis of hydrogen chloride?

19. What chemical law is illustrated in the synthesis of hydrogen chloride? What other experiment have we had which illustrates the same law?

20. Why is the ocean salty?

21. Calculate the percentage composition of hydrogen chloride.

22. How many grams of sodium chloride are needed to yield, with sulfuric acid, 30 grams of hydrogen chloride?

23. If the gas in Problem 22 is dissolved in water, making a 30% solution whose density is 1.15 grams per cubic centimeter, how many cubic centimeters of hydrochloric acid will be produced?

Topic for Further Study

The manufacture of hydrochloric acid. What is the commercial method of preparing hydrochloric acid? What raw materials are used? What is the by-product? Of what is the apparatus built? Why? Consult a book on Industrial Chemistry (Thorp or Rogers).

CHAPTER XIII

ACIDS, BASES, AND SALTS

Acids in general — bases — sodium hydroxide, preparation, properties, and uses — neutralization of base and acid — molar and normal solutions of a base and acid — naming acids, bases, and salts.

148. Acids in general. Hydrochloric acid is an example of the large class of substances known as **acids,** all of which contain hydrogen. In a dilute water solution the hydrogen can be liberated by certain metals, the action being a case of replacement. Some substances, like sugar, contain hydrogen, which cannot be replaced by metals; they are therefore not acids. *Water solutions of all acids have a peculiar sour taste, and all turn a certain natural dye, called litmus, from* ***blue to red.*** Some of the commoner acids, beside hydrochloric and sulfuric, are nitric (HNO_3), acetic (which gives vinegar its sour taste), and citric acid (which is one of the acids present in lemons).

Another characteristic of acids is their rapid reaction with certain compounds known as *bases.*

149. Bases. We saw (§ 36) that when sodium reacts with water, hydrogen and a compound called sodium hydroxide (NaOH) are formed. This compound is soluble in water, and when its water solution is evaporated, it is left as a white solid. Sodium hydroxide, known commercially as "caustic soda," is a typical base. Certain soluble bases (NaOH and KOH) are called **alkalies.** *Water solutions of bases have a peculiar bitter, or caustic, taste and a smooth, soapy feeling. They change* ***red litmus to blue,*** which is the reverse of the change caused by

acids. They all contain oxygen and hydrogen, a combination of atoms called the **hydroxyl group** (**OH**).

150. Caustic soda, or sodium hydroxide (NaOH). Large quantities of caustic soda are made by the electrolysis of a concentrated solution of sodium chloride. This process may be expressed thus:

$$\underset{\text{sodium chloride}}{2\,NaCl} \longrightarrow \underset{\text{sodium}}{2\,Na} + \underset{\text{chlorine}}{Cl_2} \quad \text{(electrolysis)}$$

$$\underset{\text{sodium}}{2\,Na} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{hydrogen}}{H_2}$$

We have already seen (§ 132) that this is the industrial process for preparing chlorine, and that sodium hydroxide is a valuable by-product. If this process is carried out in one vessel, the sodium hydroxide gradually diffuses back to the other electrode and reacts with the chlorine

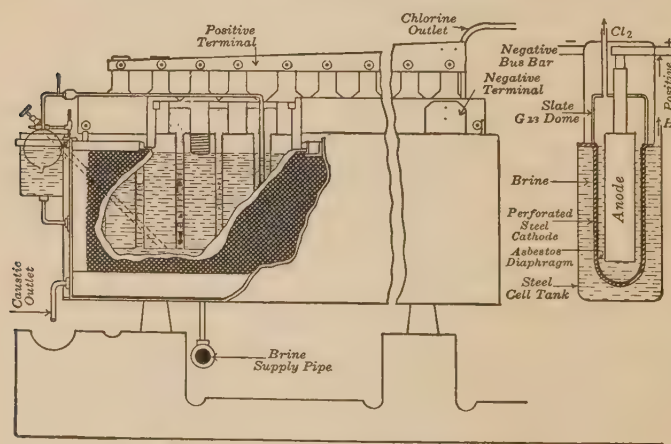


Fig. 81. Electrolytic cell for decomposing salt.

to form products which are not desired. Several different devices have been invented to obviate this difficulty. Perhaps the simplest of these involves the separation of the two electrodes by means of porous asbestos, as shown in figure 81. The carbon rods act as anodes and the perforated steel diaphragm as the cathode. A concentrated solu-

tion of salt is fed in near the positive electrode, and the sodium hydroxide solution, which is formed near the other electrode, is continually drawn off. The solution of sodium hydroxide is then evaporated at a high temperature and leaves sodium hydroxide in a molten condition. This can be cast into any desired shape.

In some factories, such as paper mills, both bleaching powder and caustic soda are employed, and so immediate use can be made of all the products of this electrolysis of sodium chloride except the hydrogen. The chlorine produced at the anode is passed directly into calcium hydroxide to form "bleach."

151. Properties and uses of sodium hydroxide. This substance is a white, brittle solid, which for laboratory purposes is ordinarily sold in slender sticks, but for industrial uses as a solid mass in iron drums. It rapidly absorbs water and carbon dioxide from the air. It is extremely soluble in water. Its solutions are used whenever a base is needed in the laboratory.

Concentrated solutions of sodium hydroxide and the moistened solid itself are very corrosive, hence the name **caustic soda.** It will quickly disintegrate most vegetable and animal material. In the household, it is valuable for cleansing purposes because it reacts with and dissolves grease; it is sold in tin cans under the name **lye.** Sodium hydroxide is a very important substance in the industries; it is used in the manufacture of hard soaps, and of paper and cotton goods, in the refining of petroleum, and in the preparation of coal-tar products. (See Industrial Chart on page 181.)

152. Neutralization of base and acid. When a base and an acid are brought together in solution in just the right proportion, the characteristic properties of each disappear. It is evident that there has been a chemical change. The base and the acid are said to neutralize each other, and the process is called **neutralization.** To determine just when the right amount of acid has been used to neutralize a given amount of

base, we use litmus or some other **indicator** * like phenolphthalein.

If we allow 10 cc. of hydrochloric acid to run from a burette (Fig. 82) into a beaker, and add a drop or two of litmus, the solution becomes bright red. A dilute solution of sodium hydroxide is now added little by little from the other burette, and the solution is stirred. When a certain amount of the base has run in, the color of the solution suddenly turns blue. This shows that slightly too much base has been added. A few drops of acid will restore the red color, and a few drops more of the base will again make the solution blue. When the solution is at a point where a drop of either acid or base will reverse the process, the right proportions of acid and base are present. This is called the **end point.** Burettes are used in such an experiment so that the amount of acid and base employed may be accurately measured. If the solution is now evaporated, little cubes of a white solid will be found, which is common salt.

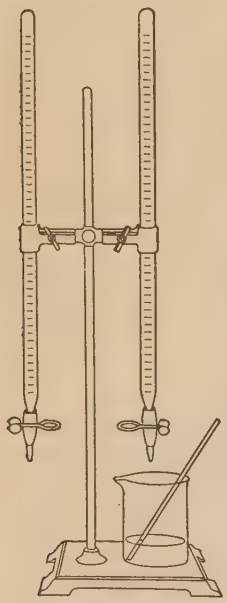


Fig. 82. Neutralization of an acid by a base.

By the reaction of sodium hydroxide and hydrochloric acid, sodium chloride and water have been formed. The sodium chloride is soluble in water and can be found only by evaporation. The equation for this important reaction is:

BASE		ACID		SALT		WATER
$NaOH$	+	HCl	$\longrightarrow$	$NaCl$	+	H_2O
sodium hydroxide		hydrochloric acid		sodium chloride		water

Sodium chloride (common salt) is an example of a very large and important group of compounds known as **salts.** The process of neutralization always produces a salt and water. It should be noted that the metal of the base and the non-

* An indicator is a substance which shows one color in an acid and another in a base solution.

hydrogen part of the acid are united in the salt. *The compounds formed by the replacement of the hydrogen of an acid by a metal are called* ***salts.***

153. Application of neutralization to analysis. If we know the concentration of the basic solution, that is, the number of grams of sodium hydroxide per liter of solution, we can quickly determine the concentration of the acid used to neutralize the basic solution by merely measuring the volumes of the solutions.

From what we have already learned (§ 124), we know from the following equation that 40 grams of sodium hydroxide will react with 36.5 grams of hydrogen chloride:

$$\underset{40\text{ g.}}{NaOH} + \underset{36.5\text{ g.}}{HCl} \longrightarrow NaCl + H_2O$$

Therefore, if we have a liter of sodium hydroxide solution containing 40 grams of sodium hydroxide and a liter of acid solution containing 36.5 grams of hydrogen chloride, and mix these solutions, there will be no excess of acid or base. Obviously it is not necessary to use all of both solutions to obtain a neutral reaction. We have only to take equal volumes of each (for example, 10 cc. of the acid and 10 cc. of the base) and these solutions will neutralize each other. Solutions which contain the formula weight of a compound in grams in 1000 cc. of the solution are called **molar solutions.**

Let us suppose we start with a molar solution of sodium hydroxide and wish to determine the concentration of an unknown hydrochloric acid solution. We determine as in the above experiment, using burettes and an indicator, how much of the molar sodium hydroxide is required to neutralize the given amount of the acid. If 25 cc. of sodium hydroxide neutralizes 25 cc. of the acid, of course the hydrochloric acid is of the same concentration as the base, that is, it is also molar. If only 2.5 cc. of sodium hydroxide are required, the hydrochloric acid must be much less concentrated than the base, in fact, only one-tenth molar. If 50 cc. of sodium hydroxide are required for 25 cc.

of acid, we would conclude that there are twice as many molecules of acid in the given solution as of base, that is, that the acid is 2 molar. Thus we see that *the volumes of basic and acid solutions required for neutralization vary* ***inversely*** *as the concentration of the solutions.* This process of determining the concentration of an unknown acid or base is called **titration.**

154. Normal solution. As long as our acid and base are like hydrochloric acid and sodium hydroxide, we have no difficulty in using the idea of a molar solution. But some acids, like sulfuric acid (H_2SO_4), neutralize 2 molecules of base:

$$\underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{sulfuric acid}}{H_2SO_4} = \underset{\text{sodium sulfate}}{Na_2SO_4} + \underset{\text{water}}{2\,H_2O}$$

Thus, 10 cc. of a molar solution of sulfuric acid require 2 times 10 or 20 cc. of a molar solution of sodium hydroxide for neutralization. It is convenient to have acid and basic solutions so that equal volumes will neutralize each other. This can be done if we use **normal solutions.** *A normal acid solution contains 1 gram of replaceable hydrogen per liter of the solution* (not the solvent), and *a normal base solution contains 17 grams of the hydroxyl (OH) group per liter of the solution.* It will be seen that in the case of an acid with one replaceable hydrogen atom and of a base with one hydroxyl group a normal solution is the same thing as a molar solution. In the case of acids with 2 hydrogen atoms we must have only half the formula weight in a liter for a normal solution. If the acid had three hydrogen atoms, we should take only a third of a formula weight. Similarly a normal solution of calcium hydroxide ($Ca(OH)_2$) would contain $\frac{74}{2}$ or 37 grams in one liter.

The common abbreviation for a molar solution is M, for a normal solution is N. We thus speak of a tenth normal solution as $\frac{N}{10}$ or 0.1 N; a 2 molar solution is 2 M.

155. Naming of bases, acids, and salts. The chemist writes formulas, but *does not talk formulas*. Hence it is necessary to pay close attention to the method of naming chemical compounds, for a very slight change in the name of a compound will often transform it into a compound of quite different properties. For example, mercuric chloride ($HgCl_2$) is corrosive sublimate, which is extremely poisonous; but mercurous chloride (HgCl) is calomel, which is a common medicine.

In naming **bases,** we simply prefix the name of the metal to the word *hydroxide*. Thus we have sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), and aluminum hydroxide ($Al(OH)_3$).

In naming **acids,** we must distinguish between an acid consisting of two elements (a *binary acid*) and an acid consisting of three elements (a *ternary acid*). In the binary acid we have but one element beside the hydrogen; here we prefix **hydro-** to the name of the second element and add the termination **-ic.** Thus we have hydrochloric acid (HCl) and hydrosulfuric acid (H_2S). The large majority of ternary acids contain oxygen as the third element. It often happens that the same three elements form more than one acid. The most familiar one is named from the characteristic element and ends in the suffix **-ic;** while the one with less oxygen has a similar name, but the ending is the suffix **-ous.** Thus we have sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3); also nitric acid (HNO_3) and nitrous acid (HNO_2).

In naming a **salt,** we have to consider very carefully the acid from which it has been derived. If the acid is binary, then the salt is named after its two constituent elements with the ending **-ide.** Thus we have sodium chloride (NaCl), zinc chloride ($ZnCl_2$), and copper sulfide (CuS). If the acid is ternary and its name ends in **-ic,** then the name of the salt ends in **-ate;** but if the ternary acid ends in **-ous,** then the name of the salt ends in **-ite.** This will be made clear in the table on page 144.

Name of Acid	Formula	Name of Salt	Formula
Hydrochloric	HCl	Sodium chloride	$NaCl$
Sulfuric	H_2SO_4	Copper sulfate	$CuSO_4$
Sulfurous	H_2SO_3	Potassium sulfite	K_2SO_3
Hydrosulfuric	H_2S	Zinc sulfide	ZnS
Nitric	HNO_3	Potassium nitrate	KNO_3
Nitrous	HNO_2	Sodium nitrite	$NaNO_2$

With acids like sulfuric and sulfurous that have two replaceable hydrogen atoms, we can have salts in which only one of the hydrogen atoms is replaced by a metal. Such salts are sometimes called *acid* salts, and the prefix bi- is employed in naming them. Thus, sodium bisulfate ($NaHSO_4$), sodium bisulfite ($NaHSO_3$), sodium bicarbonate ($NaHCO_3$) are examples.

SUMMARY OF CHAPTER XIII

ACIDS contain hydrogen, which can be replaced by a metal. Their water solutions turn litmus red and usually have a sour taste.

A BASE is the hydroxide of a metal or a metallic radical. Sodium and potassium hydroxides are typical bases, which may be prepared by the electrolysis of the chloride solutions. Their water solutions turn litmus blue and neutralize acids.

SALTS are the compounds produced by the replacement of the hydrogen of an acid by a metal or metallic radical. A salt and water are produced by the neutralization of a base by an acid.

A MOLAR SOLUTION contains the formula weight in grams per liter of solution of a compound.

A NORMAL SOLUTION of an acid contains 1 gram of hydrogen per liter of solution. A normal solution of a base contains 17 grams of the hydroxyl group per liter of solution.

THE NAME OF A BASE consists of the name of the metal and the word *hydroxide*.

IN NAMING AN ACID, the names of both elements and the ending *ic* are used for binary acids, and for the commoner ternary acid the name of the characteristic element and the ending *ic* are used. But for the ternary acid containing less oxygen the ending *ous* is added.

IN NAMING SALTS, a binary salt includes the names of both elements with the ending *ide*. Those ternary salts derived from *ic* acids end in *ate*, and those derived from *ous* acids end in *ite*.

Ate and *ite* are endings for nouns; *ic* and *ous* are endings for adjectives.

Questions and Problems

1. Name six acids and write the formula for each.
2. Name four characteristics of acids.
3. Name six foods which you think may contain acids.
4. How could you determine whether a bottle labelled HCl contained concentrated or dilute hydrochloric acid?
5. How does a base differ from an acid?
6. What is the principal ingredient of a can of household lye?
7. Household ammonia (NH_4OH) is sometimes called the volatile alkali. Why?
8. Glass stoppers in bottles of sodium hydroxide often stick as if cemented into the bottle. Explain.
9. How may chemically pure (C.P.) common salt be prepared in the laboratory?
10. What compound is always formed in the neutralization of a base and acid?
11. Complete and balance the following equations, and underwrite the names of the various substances:

(*a*) $KOH + HCl \longrightarrow$

(*b*) $NaOH + H_2SO_4 \longrightarrow$

(*c*) $NaOH + HNO_3 \longrightarrow$

(*d*) $NaOH + H_3PO_4 \longrightarrow$

(*e*) $KOH + H_2CO_3 \longrightarrow$

12. How would you prove that a given solution contained a chloride?

13. What weight of potassium hydroxide (KOH) will be needed to make up one liter of a normal solution?

14. What weight of phosphoric acid (H_3PO_4) is required to make up a liter of a normal solution?

15. Express the concentration of a 5 per cent aqueous solution of sodium hydroxide (density 1.05 g. per cc.) in terms of a normal hydroxide solution.

16. If 45 cc. of normal sodium hydroxide solution were required to neutralize 25 cc. of hydrochloric acid, (*a*) what would be the normal concentration of the acid? (*b*) What would be its concentration in grams per liter?

17. If all of the sodium chloride in a solution is precipitated by 17 grams of silver nitrate ($AgNO_3$), how much sodium chloride was present in the solution?

18. A certain weight of sodium hydroxide was neutralized with hydrochloric acid. The solution was evaporated and the residue, sodium chloride (NaCl), weighed 11.7 grams. Compute the weight of (*a*) sodium hydroxide and (*b*) of hydrochloric acid.

CHAPTER XIV

MOLECULAR WEIGHTS AND THEIR USES

Uniformity of gases — Avogadro's theory — its consequences — hydrogen molecule has two atoms — problems involving volumes of gases only — molecular weights — gram-molecular volume — problems on volumes of gases.

156. Uniformity of gases. Careful experiments show that all gases behave alike as regards the effects of pressure. Thus, *the volume of any gas varies inversely as the pressure if the temperature remains the same,* according to BOYLE'S LAW. Experiments also show that all gases behave alike as regards the effects of temperature. Thus, *the volume of any gas varies directly as the absolute temperature if the pressure remains the same,* according to the LAW OF CHARLES.*

In Chapter V we learned from the volumetric synthesis of steam that

2 vol. hydrogen + 1 vol. oxygen ⟶ 2 vol. steam

In Chapter XI we have just seen that

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vol. hydrogen chloride

A careful study of the process of making ammonia gas by the direct union of hydrogen and nitrogen gives these results:

3 vol. hydrogen + 1 vol. nitrogen ⟶ 2 vol. ammonia

These experimental facts all illustrate the LAW OF GAY-LUSSAC:

* At this point some teachers will wish to review the gas laws as outlined in the Appendix.

The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.

157. Avogadro's explanation. These striking cases of uniformity in the behavior of gases led the famous Italian, Avogadro (Fig. 83), in 1811 to the following explanation: He assumed that *equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.* In other words, 1 cubic centimeter of hydrogen has just as many molecules as 1 cubic centimeter of oxygen, nitrogen, chlorine, hydrogen chloride, or any other gas, provided the conditions of temperature and pressure are the same.

Fig. 83. Amedeo Avogadro (1776–1856). Professor of physics at Turin, Italy.

158. Consequences of this theory. It should be noticed at once that this theory makes no assumption as to the *actual* number of molecules in a cubic centimeter. But it does give us a simple method of comparing the weights of molecules of gas by comparing the densities of the gases, that is, their weights per unit volume. We can best show this in a table:

Gas	Density (Grams per liter)	Relative Weights of Molecules
Hydrogen	0.09	1
Oxygen	1.43	16
Nitrogen	1.25	14
Hydrogen chloride	1.64	18.2

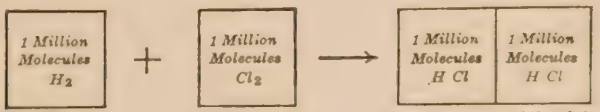
In this table we have used only the approximate values for densities and have taken hydrogen as the basis of comparison. It will be seen that the third column gives us the relative weights of the molecules referred to the hydrogen molecule as a standard.

159. Hydrogen molecule has two atoms. Another very interesting conclusion that we draw from Avogadro's theory is that *every molecule of hydrogen has at least two atoms.* Let us see why this is so. Our experiment in the synthesis of hydrogen chloride showed that

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vol. hydrogen chloride

According to Avogadro we must assume that we have the same number of molecules of hydrogen as of chlorine and *twice* that number of molecules of hydrogen chloride. Suppose we have a million molecules of hydrogen; then we must have a million molecules of chlorine and *two* million molecules of hydrogen chloride. Each one of these molecules of hydrogen chloride must contain at least one atom of hydrogen; so that we have in all *two million* **atoms** of hydrogen coming from *one million* **molecules** of hydrogen. This experiment indicates that **each molecule of hydrogen contains at least 2 atoms of hydrogen** (H_2).

It may help us to picture this relation if we draw squares to represent the equal volumes, as shown below:



Hydrogen Chlorine Hydrogen chloride

By a similar course of reasoning it follows that the chlorine molecule also contains at least two atoms.

We represent these facts by the following equation:

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

This means that one molecule of hydrogen, containing 2 atoms, plus one molecule of chlorine, containing 2 atoms, gives 2 molecules of hydrogen chloride, each containing one atom of hydrogen and one atom of chlorine.

NOTE. It should be remembered that any *even* number might be used instead of two; but since there is no reaction in which the hydrogen molecule appears to be divided into more than two parts, we decide that there must be *only* two atoms in the molecule.

From a consideration of the volumetric synthesis of steam, we come by similar reasoning to the conclusion that the oxygen molecule contains two atoms (O_2); and from a study of the synthesis of ammonia, we conclude that the nitrogen molecule also contains two atoms (N_2).

160. Problems involving volumes of gases. One of the practical advantages which results from writing our equations involving the reaction of gases *in molecular form* is that it gives us a very simple method of computing the volumes of the gases involved.

FOR EXAMPLE, suppose we wish to find the volume of oxygen needed to burn 1 liter of carbon monoxide.

We first write the equation

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

Since equal numbers of molecules of gases occupy equal volumes (Avogadro's Principle), we may read the equation thus:

$$2 \text{ vol. } CO + 1 \text{ vol. } O_2 \longrightarrow 2 \text{ vol. } CO_2$$

Therefore 1 liter of carbon monoxide (CO) will require one-half a liter or 500 cc. of oxygen and will form 1 liter of carbon dioxide (CO_2).

RULE. *In the case of gases the* ***coefficients*** *of formulas in equations represent the* ***relative volumes*** *of the substances.*

PROBLEMS

1. The equation for the reduction of carbon dioxide with red-hot carbon is as follows:

$$CO_2 + C \longrightarrow 2\,CO$$

and the equation for burning carbon monoxide is:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

(*a*) What volume of carbon monoxide will be produced by the reduction of 100 liters of carbon dioxide?

(*b*) What volume of oxygen is needed to burn the carbon monoxide produced in problem (*a*)?

2. When 150 cc. of hydrogen burn in chlorine, how many cubic centimeters of hydrogen chloride are produced?

3. When acetylene burns completely, the chemical action is expressed by the following equation:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$$

(*a*) When 10 liters of acetylene gas are burned, how many liters of oxygen are required?

(*b*) How many liters of carbon dioxide are produced?

4. At very high temperatures it is possible to form nitric oxide (NO) by direct combination of nitrogen and oxygen according to the following equation:

$$N_2 + O_2 \longrightarrow 2\,NO$$

How many cubic feet of air will be needed to produce 100 cubic feet of nitric oxide? (Assume air to be one-fifth oxygen.)

5. Alcohol (C_2H_5OH) vapor when it is completely burned in oxygen produces carbon dioxide and water vapor according to the following equation:

$$C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$$

(*a*) How many liters of oxygen will be required to burn 10 liters of alcohol vapor?

(*b*) How many liters of carbon dioxide will be produced in this process?

161. Standard of molecular weights. We have just seen that the molecule of oxygen contains two atoms (O_2). It has also been stated (§ 94) that chemists have agreed to take as their standard for atomic weight the atomic weight of oxygen 16.000. It follows then that *the molecular weight of oxygen is exactly 32.000, and this is the standard of molecular weights.* Thus, if we know the formula of a gaseous substance, we can at once compute its molecular weight by adding the weights of its atoms. For

example, the formula for hydrogen chloride is HCl, therefore its molecular weight is 1.008 + 35.46 or 36.468; the formula for acetylene is C_2H_2, and its molecular weight is $2 \times 12.00 + 2 \times 1.008$ or 26.016.

162. Gram-molecular volume. The chemist often has occasion to use as many grams of a gas as there are units in its molecular weight, and so he calls this weight the **gram-molecular,** or **molar, weight.** Thus, 32 grams is the gram-molecular, or molar, weight of oxygen.

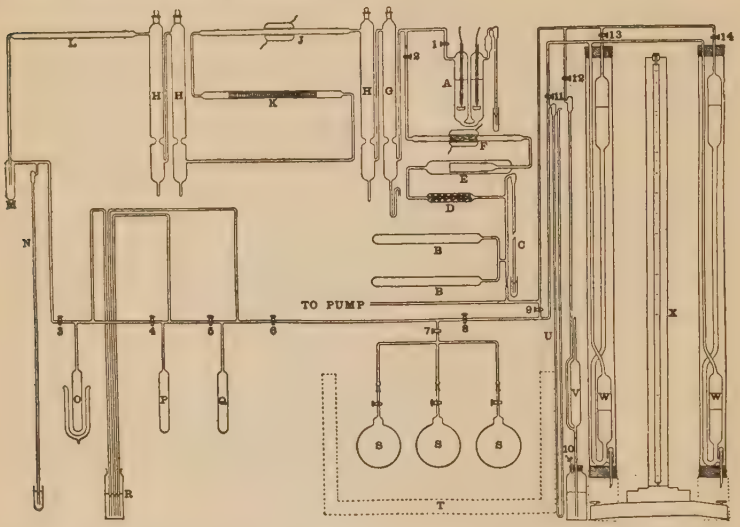


Fig. 84. Apparatus for determining the density of oxygen as used by Baxter and Starkweather. Their value is 1.42901 grams per liter.

The oxygen was generated either by electrolysis in cell A or by heating potassium chlorate in B, B. The gas is purified by passing through tubes D–L. In some experiments the gas was further purified by liquefaction and fractional distillation in tubes O, P, Q. The gas was finally passed into the exhausted globes S, S, S (surrounded by ice-water) at a pressure measured by the gauges on the right. The globes were finally sealed off and weighed.

What volume does 32 grams of oxygen occupy under standard conditions? Since one liter of oxygen weighs approxi-

mately 1.43 grams (Fig. 84), it follows that it takes $\frac{32}{1.43}$ or 22.4 liters of oxygen under standard conditions to weigh 32 grams. If we divide the gram-molecular weight of *any gas* by its density, we always get 22.4 liters. Therefore we conclude that *the gram-molecular weight of any gas occupies a volume of 22.4 liters.*

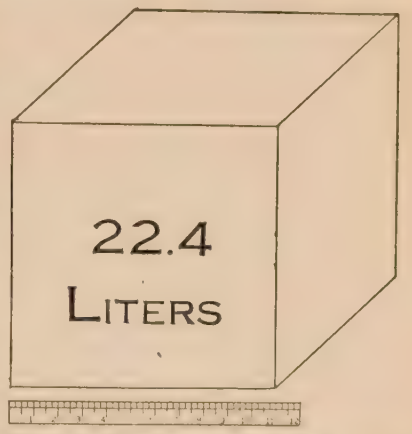


Fig. 85. Cube representing one gram-molecular volume.

This gaseous volume of 22.4 liters (Fig. 85) is one of great importance to the chemist in the laboratory, for it furnishes him a quick means of calculating the molecular weight of any substance which can be weighed in the gaseous state: all he has to do is to compute from the weight of a given volume under standard conditions what 22.4 liters would weigh in grams. Therefore we conclude that *the weight in grams of 22.4 liters of any gas (at 0° C. and 760 mm.) is equal to the molecular weight of the gas.*

For example, carbon dioxide weighs approximately 1.98 grams per liter; therefore 22.4 liters would weigh 22.4 × 1.98 or about 44 grams. The molecular weight of carbon dioxide is, then, approximately 44.

Again, nitrogen weighs 1.25 grams per liter; therefore 22.4 liters would weigh 22.4 × 1.25 or about 28 grams. The molecular weight of nitrogen is, then, approximately 28.

Problems

1. If 500 cc. of marsh gas under standard conditions weighs 0.358 grams, what is the molecular weight of marsh gas?

2. Given the formula of carbon monoxide as CO: compute its density (grams per liter) under standard conditions.

3. Find the molecular weight of a gas of which 150 cc. at 18° C. and 752 mm. weigh 1.50 grams. (See Appendix for gas laws.)

4. If the molecular weight of nitrous oxide is 44, what is the approximate density (grams per liter) of the gas?

5. From the table of densities of gases given in the Appendix, compute the molecular weights of the following gases: (*a*) acetylene; (*b*) ammonia; (*c*) carbon monoxide; (*d*) hydrogen sulfide; and (*e*) sulfur dioxide.

6. The density of helium is 0.178 grams per liter under standard conditions, and its atomic weight is 4.00. How many atoms does a helium molecule contain?

163. Problems involving weight and volume. Those problems which involve *both* the weights of solid or liquid substances and the volumes of gases used or produced in a chemical reaction can be easily solved by means of the gram-molecular volume.

FOR EXAMPLE. How many liters of carbon dioxide under standard conditions can be obtained from 2 kilograms of marble by the action of hydrochloric acid?

Let us proceed in the regular way used in the problems involving only weights.

(1) Write the complete equation.

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

(2) Write above the actual weight and volume.

$$\begin{array}{l} \text{2000 g.} \qquad\qquad\qquad\qquad\qquad\quad x \text{ liters} \\ CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2 \end{array}$$

(3) Underneath write the formula weight and gram-molecular volume.

$$\begin{array}{l} \text{2000 g.} \qquad\qquad\qquad\qquad\qquad\quad x \text{ liters} \\ CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2 \\ \quad 100 \qquad\qquad\qquad\qquad\qquad\quad 22.4 \end{array}$$

(4) Make the fractional equation.

$$\frac{2000}{100} = \frac{x}{22.4}$$

(5) Solve. $100\,x = 2000 \times 22.4$

$$x = \frac{2000 \times 22.4}{100} = \textbf{448 liters.} \quad \text{Answer.}$$

CHECK: Since 2000 grams is 20 times 100, we should expect the answer to be about 440 liters.

164. Another illustrative problem on weight and volume. How many grams of magnetic oxide of iron (Fe_3O_4) can be reduced by 10.0 liters of hydrogen under standard conditions?

$$\underset{\substack{(168+64)\\232}}{\overset{x\text{ g.}}{Fe_3O_4}} + \underset{(4\times 22.4)\ \ 89.6}{\overset{10\text{ liters}}{4\,H_2}} \longrightarrow 3\,Fe + 4\,H_2O$$

$$\frac{x}{232} = \frac{10}{89.6}$$

$$x = \frac{10 \times 232}{89.6} = \mathbf{25.9\ g.}\quad \text{Answer.}$$

CHECK: Since 10 liters is about $\frac{1}{9}$ of 89.6 liters, we should expect x to be about 25 g.

NOTE. Under the *solids* and *liquids* we write the formula weights as usual; but under *gases* we write the number of liters, which is the number of molecules times 22.4.

PROBLEMS

1. What weight of zinc will be needed to generate 100 liters of hydrogen (measured at 0° C., 760 mm.), if dilute sulfuric acid is used?

2. What weight of zinc will be needed to generate the same volume of hydrogen, if dilute hydrochloric acid is used?

3. What volume of hydrogen (measured under standard conditions) could be obtained by the electrolytic decomposition of 5 grams of water?

4. What volume of hydrogen (measured under standard conditions) is needed to reduce 10 grams of copper oxide (CuO)?

5. What volume of carbon dioxide (measured under standard conditions) would be given off from 1 kilogram of sodium bicarbonate in a fire extinguisher? The equation is

$$2\,NaHCO_3 + H_2SO_4 \longrightarrow 2\,CO_2\uparrow + 2\,H_2O + Na_2SO_4$$

6. What weight of zinc is required to make 10 liters of hydrogen at 15° C. and 745 mm. by replacement from sulfuric acid?

7. What weight of pure carbon will have to be burned to produce 44.8 cc. of carbon dioxide under standard conditions?

SUMMARY OF CHAPTER XIV

UNIFORM BEHAVIOR OF ALL GASES:

The volume of any gas varies inversely as the pressure if the temperature remains the same (Boyle's Law).

The volume of any gas varies directly as the absolute temperature if the pressure remains the same (Law of Charles).

The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers (Law of Gay-Lussac).

AVOGADRO'S THEORY: Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.

As a *consequence* of this theory we conclude that molecules of hydrogen, oxygen, nitrogen, and chlorine have *two* atoms each.

RELATIVE VOLUMES OF GASES are represented by the coefficients of their molecules in an equation.

MOLECULAR WEIGHT of a substance is the number which expresses the weight of its molecule compared with the oxygen molecule as 32.

GRAM-MOLECULAR WEIGHT of any gas occupies a volume of 22.4 liters.

MOLAR WEIGHT = weight in grams of 22.4 liters of a gas under standard conditions.

Questions

1. State the facts and theories which lead us to believe that the oxygen molecule contains two atoms.

2. State approximately the relative number of molecules of nitrogen and oxygen in the atmosphere.

3. What are the facts and theories which lead us to believe that the nitrogen molecule contains two atoms?

4. What assumption about temperature and pressure is made in the Law of Gay-Lussac?

5. Arrange the gases having the following formulas in the order of decreasing density: (*a*) NH_3; (*b*) CO; (*c*) CH_4; (*d*) He; and (*e*) NO.

CHAPTER XV

SULFUR AND THE SULFIDES

Occurrence of sulfur — production — experiments — properties — allotropic forms — chemical behavior — use of sulfur in manufacture of rubber.

Occurrence of hydrogen sulfide — preparation — properties — analytical uses. Carbon disulfide.

165. Importance and occurrence of sulfur. The element sulfur has been known since the earliest times. Mixed with saltpeter (KNO_3) and charcoal (C), sulfur has long been used in black gunpowder. Sulfur enters into the lime-sulfur mixtures used for spraying shrubs and trees; it furnishes the sulfur dioxide for bleaching, disinfecting, and refrigeration. Recent experiments show that wood, such as railway ties, may be made to absorb molten sulfur, which preserves the wood and renders it acid resistant. Perhaps the most important of all is its use in the manufacture of sulfuric acid, a substance which plays a large and essential rôle in the preparation of other chemicals.

Large deposits of free sulfur occur in Sicily, Texas, and Louisiana. It is frequently found around the rims of craters and in the vicinity of volcanoes, as well as in non-volcanic regions. There are large deposits of sulfur compounds, such as the sulfides of metals: **iron pyrite,** or fool's gold (FeS_2), **galena** (PbS), and **zinc blende** (ZnS); also the sulfates, such as **gypsum** ($CaSO_4 \cdot 2\,H_2O$).

166. Industrial production. In America the deposits of sulfur are from 500 to 1500 feet below the surface of the ground; and because of the surrounding clay, quicksand, and rock, it is impossible to mine it by the usual methods. An American

chemist, Herman Frasch, after ten years of labor worked out a most ingenious and successful method of getting this sulfur. The process is essentially this: A hole is drilled down to the bottom of the sulfur bed. Into this hole is lowered a six-inch iron pipe which contains two smaller pipes, one within the other (Fig. 86). Water heated under pressure to a temperature well above its boiling point (170° C.) is forced down through the six-inch pipe. On coming into contact with the sulfur, the hot water melts it and turns the underground deposit into a subterranean lake of molten sulfur. Compressed hot air is now forced down through the smallest pipe and forms a froth with the molten sulfur and hot water. The pressure of the hot water and compressed air forces this froth up through the middle pipe, whence it discharges into a large wooden vat which measures about 150 by 250 feet. In this way great quantities of sulfur can be melted and blown to the surface. It is very pure (about 99 per cent); and after it has solidified, the huge blocks are broken up, loaded directly into cars (Fig. 87), and shipped to various points for use without further purification. Sometimes a block contains over a million tons of sulfur.

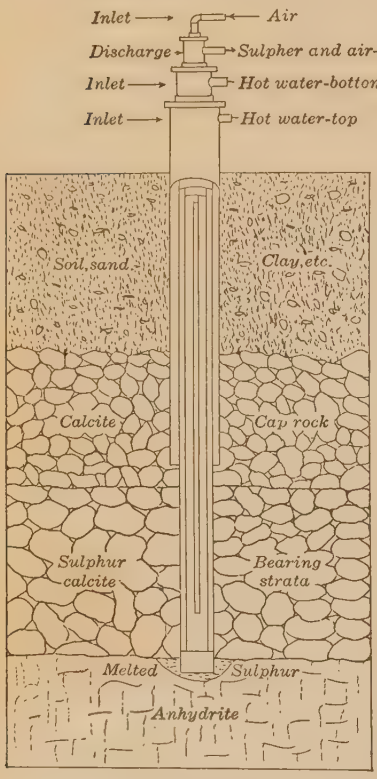


Fig. 86. Method of piping in the Frasch process.

Fig. 87. Pouring molten sulfur into bins and loading solid sulfur into cars.

167. Properties of sulfur. Sulfur is a pale yellow, brittle solid about twice as heavy as water. It is not soluble in water and has no marked taste or odor. When heated it melts at 114° C. to a straw-colored liquid; as the temperature rises, the liquid becomes darker and more and more viscous until at about 235° C. it is almost black and too thick to run out of the vessel. Then it grows thinner again on further heating and boils at 445° C. As a solid it is a very good insulator of heat and electricity.

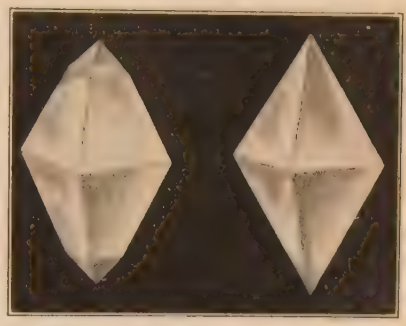


Fig. 88. Rhombic form of sulfur.

168. Three varieties of sulfur. If we dissolve some roll sulfur in a small quantity of carbon disulfide (CS_2) and then pour the solution into a crystallizing dish, the solvent slowly evaporates and leaves the sulfur in the shape of small crystals.

If this experiment is carried out on a larger scale and with certain precautions, more perfectly shaped crystals will be formed, like the ones shown in figure 88. These crystals generally have 8 sides (octahedral) and belong to the rhombic system; hence this variety is called **rhombic sulfur.** The free sulfur found in nature is rhombic. Roll sulfur and flowers of sulfur are largely composed of very small crystals of this sort.

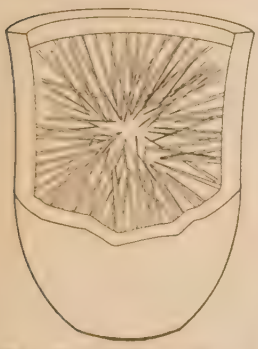


Fig. 89. Prismatic or needle-shaped crystals formed in a crucible.

Another crystalline variety can be obtained by first melting some sulfur and then allowing it to cool slowly. This can be conveniently done in a clay crucible. As the melted sulfur begins to solidify, a thin crust forms over the surface. If a hole is broken through and the

liquid sulfur underneath is poured out, a loose mass of needle-like crystals (Fig. 89) is found to fill the interior of the crucible.

These crystals which grow in the liquid sulfur are of the monoclinic, or **prismatic**, variety. They are long, transparent, pale-yellow needles, almost rectangular in cross section and beveled at the points. Sulfur can be kept in this form indefinitely, provided the temperature is above 96° C. and below its melting point; but when it is allowed to cool, it slowly becomes opaque because of its change into particles of rhombic sulfur.

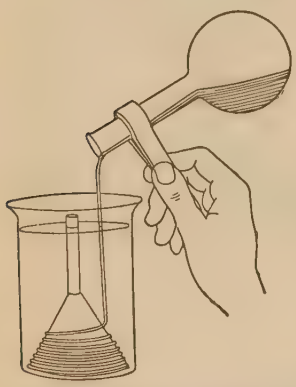


Fig. 90. Pouring melted sulfur into cold water forms plastic sulfur.

We shall now heat a quantity of ordinary roll sulfur in a small flask until it is almost boiling and then pour the hot sulfur in a thin stream into a beaker of cold water, as shown in figure 90. It is convenient to place a funnel in the beaker and pour the stream of sulfur around it. Then we may easily lift out the funnel and the solidified sulfur with it. It is no longer brittle but seems almost like a gum.

The dough-like product obtained by suddenly chilling the molten sulfur in cold water is called **plastic** sulfur. Since it has no crystalline form it is also called **amorphous** sulfur. This variety is unstable and in the course of a few days changes into the rhombic form. The crystalline forms of sulfur are soluble in carbon disulfide; the amorphous forms are not.

There are a number of other forms in which elementary sulfur can exist, but we shall not discuss them here.

169. Allotropic forms. The different modifications of an element, such as we have described for sulfur and such as exist also for other elements like carbon and oxygen, are called **allotropic forms.** It must not be thought, however, that the sulfur atom itself is different in these variations. The differences in

form are due to the number of atoms which are combined in the sulfur molecule, and perhaps also to the way in which the atoms are grouped together. In the case of sulfur we do not yet know just how many sulfur atoms there are in the molecule of each of the different modifications; but we do know that sulfur atoms have a tendency to form large molecules, since gaseous sulfur contains a molecule which has eight atoms. In the case of the allotropy of oxygen it has been found that the difference is due solely to the fact that one form has two atoms to the molecule (O_2), while the other form (ozone) has three (O_3).

170. Chemical behavior of sulfur. All forms of sulfur behave very much alike chemically. When sulfur burns in the air, it yields a pungent gas, sulfur dioxide (SO_2). Most metals when heated with sulfur unite with it directly, forming metallic sulfides.

Among the first chemical reactions which we investigated were those between zinc, iron, copper, and sulfur, forming the various sulfides. The equations for these reactions are:

$$Zn + S \longrightarrow ZnS$$
$$Fe + S \longrightarrow FeS$$
$$Cu + S \longrightarrow CuS$$

Fig. 91. Gathering the latex from a rubber tree in Sumatra.

171. Use of sulfur in making rubber. The India-rubber tree (Fig. 91), chiefly grown in the tropics, furnishes a milky juice (latex), which is made into crude rubber by the addition of

acetic acid (§ 211). This material, called **caoutchouc,** is essentially a compound of hydrogen and carbon. It is soft, elastic, but unsuitable for most purposes because it very gradually oxidizes in the air and forms a brittle substance. When mixed with 10 per cent of sulfur and certain metallic compounds and then heated out of contact with the air to about 150° C., it becomes stiffer, more elastic, and much more durable. This process of **vulcanizing** produces the commercial article called rubber (Fig. 92).

Fig. 92. Making an automobile tire.

Hard rubber, also called vulcanite, is obtained when caoutchouc is mixed with from 30 to 50 per cent of sulfur and then heated to a temperature about 30 degrees higher than that applied in making the soft vulcanized rubber. Hard rubber is used in the manufacture of such articles as buttons and fountain pens; it is also a valuable insulating material for electrical machinery.

It has been found possible to prepare an **artificial rubber** which is almost identical with the natural variety. The process, however, is expensive, and the raw materials, such as potato starch or turpentine, are not cheap enough. The result is that large rubber manufacturers are laying out extensive **rubber plantations** in tropical countries in order to increase the supply of available rubber.

172. Reclaiming rubber. Much of the old rubber in automobile tires (Fig. 93) can be " reclaimed " by grinding the material into small pieces and heating it in steam-jacketed cylinders (devulcanizers) with a caustic-soda solution to destroy the cotton fiber. After it has cooked for about 20 hours under

a steam pressure of 125 pounds per square inch, the stock is washed and dried. Finally, the raw "shoddy" goes to a series of steam-heated rolls, which remove various impurities and leave about 70 per cent of the raw stock as reclaimed rubber suitable for compounding.

Fig. 93. Tires from which the rubber will be reclaimed.

Sulfides

173. Occurrence of hydrogen sulfide. This gas (H_2S) has a characteristic odor, which is recognized whenever animal substances containing sulfur become putrid. Thus, bad eggs owe their disagreeable smell to the presence of this gas. It is also found in solution in certain sulfur springs and occurs in volcanic gases.

174. Preparation of hydrogen sulfide. When hydrogen is slowly passed over melted sulfur, the two combine to form hydrogen sulfide. Even after a few minutes a trace of the gas can be detected by means of a strip of paper moistened with lead acetate ($Pb(C_2H_3O_2)_2$) solution. The paper turns dark because of the formation of lead sulfide (PbS), which is black.

The usual method of preparing hydrogen sulfide is by the action of dilute hydrochloric or sulfuric acid on iron sulfide (FeS):

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S \uparrow$$

When only a small amount of the gas is needed, the apparatus shown in figure 94 is convenient. But the Kipp generator

(Fig. 26) is better when the gas is required in larger quantities. Inasmuch as the gas is somewhat poisonous, all experiments with it should be performed either under a well-ventilated hood or in the open air.

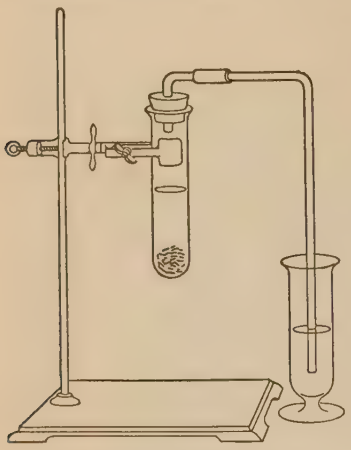


Fig. 94. Hydrogen sulfide generator.

175. Properties of hydrogen sulfide. This gas is colorless and a little heavier than air. It is fairly soluble in water, which enables us to use it in the laboratory as a solution. In pure form it acts as a poison, and even when diluted with considerable air it causes headache and nausea; but fortunately its obnoxious smell gives warning of its presence.

The gas readily burns with a bluish flame, forming water and sulfur dioxide:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When it burns in a bottle, the supply of oxygen is not sufficient to combine with both the sulfur and the hydrogen; hence the hydrogen and only a part of the sulfur burn:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

The compound is not very stable. This can be demonstrated by holding a cold porcelain dish in the hydrogen sulfide flame (Fig. 95). The dish shows a yellow spot due to the sulfur which is condensed on its surface. The gas in the interior of its own flame was decomposed by heat into its constituent elements.

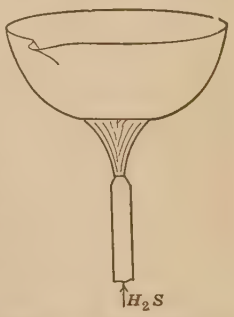


Fig. 95. Hydrogen sulfide flame deposits sulfur on a cold dish.

A water solution of the gas is a very weak acid known as **hydrosulfuric acid;** it has about the same effect on litmus paper as carbonic acid (H_2CO_3). A salt results from neutralizing hydrosulfuric acid with a base. This salt is called a **sulfide,** and can be obtained by evaporating the solution.

176. The use of hydrogen sulfide in the laboratory. Because of its action on metallic solutions, hydrogen sulfide is used as one of the reagents in analytical chemistry. The metallic sulfides which are formed have such characteristic colors that they furnish a convenient test for the presence of the metals.

Let us experiment with three solutions: (1) Dissolve a little lead acetate ($Pb(C_2H_3O_2)_2$) in some water in a test tube. (2) Dissolve a bit of white arsenic (As_2O_3) in a few drops of hydrochloric acid and then add water. (3) Dissolve a small quantity of antimony salt (tartar emetic) in water. Now pass a few bubbles of hydrogen sulfide through each solution in turn. In the first test tube we get a *black* precipitate (PbS), in the second a *yellow* precipitate (As_2S_3), and in the third a *red* precipitate (Sb_2S_3).

Thus we see that certain metallic sulfides which are insoluble in water or dilute acids can be prepared by passing hydrogen sulfide into an aqueous solution of the metallic salt.

We shall now prepare dilute solutions of copper sulfate ($CuSO_4$), iron sulfate ($FeSO_4$), and potassium sulfate (K_2SO_4), and shall then pass a few bubbles of hydrogen sulfide into each. We get a black precipitate in the copper solution and no precipitate in the other two.

If we add a few drops of ammonia water to these solutions, we get a black precipitate in the iron solution but nothing in the potassium solution.

In this experiment we note that copper sulfide (CuS) can be precipitated in an acid solution, iron sulfide (FeS) in an alkaline solution, and that potassium sulfide is precipitated in neither acid nor alkaline solutions. This furnishes a means of separating copper, iron, and potassium. The following equation will help us to understand this reaction:

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

In the case of iron sulfate we have a reversible reaction:

$$FeSO_4 + H_2S \rightleftharpoons FeS + H_2SO_4$$

The iron sulfide is acted upon by the dilute sulfuric acid. But by adding ammonia we neutralize this acid and thus allow the iron sulfide to form.

Some metals, like silver and lead, react directly with hydrogen sulfide to form the metallic sulfide. The tarnishing of silver in the household is probably due to the hydrogen sulfide which comes from slight leaks in gas pipes and from the burning of coal. Illuminating gas is supposed to be free from this gas, but it usually contains a trace of it.

177. Carbon disulfide (CS_2). We have already seen (§ 168) that this is a valuable solvent because it dissolves sulfur, rubber, and other substances which are not soluble in water. It is manufactured from coke and sulfur:

$$C + 2\,S \longrightarrow CS_2$$

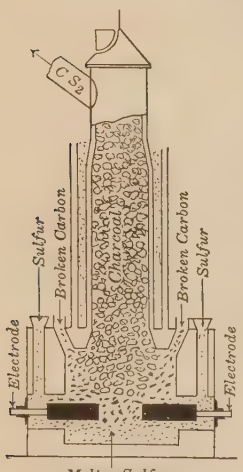


Fig. 96. Furnace for making carbon disulfide.

The reaction requires a very high temperature, which is usually obtained commercially in an electric furnace (Fig. 96). The main part is filled with coke, and the sulfur is added through the hoppers. The electric terminals are near the bottom. The heat generated vaporizes the sulfur, which unites with the hot carbon to form carbon disulfide.

Carbon disulfide is a colorless, heavy liquid, which boils at 46° C. When pure the liquid is said to have a pleasant smell, but it undergoes slight decomposition, which gives it a very disagreeable odor. It is *very inflammable. Its vapors mixed with air are explosive, and consequently no flame should be near when carbon disulfide is being used.*

Besides being valuable as a solvent, it is useful in exterminating ants and other insect pests. It has also been employed to destroy the prairie dog, as well as rats and mice.

SUMMARY OF CHAPTER XV

SULFUR is found in a free state; also in sulfides and sulfates.

In Louisiana and Texas it is melted underground by superheated water and forced to the surface.

COMMERCIALLY sulfur is sold as flowers of sulfur and as roll or lump sulfur.

ALLOTROPIC FORMS of sulfur include the rhombic, the prismatic, and the amorphous.

The *rhombic form* is the stable form; it melts at 114° C. and boils at 445° C. It is about twice as heavy as water, insoluble in water, soluble in carbon disulfide.

SULFUR BURNS in air, forming sulfur dioxide. It combines directly with a number of elements, forming sulfides.

SULFUR IS USED in the manufacture of gunpowder, lime-sulfur spray, carbon disulfide, sulfur dioxide, sulfuric acid, indurated wood, and in vulcanizing rubber.

HYDROGEN SULFIDE is formed in nature by the decay of organic matter containing sulfur; it also occurs in volcanic gases and in the water of sulfur springs.

In the *laboratory, hydrogen sulfide is prepared* by the action of dilute hydrochloric or sulfuric acid on iron sulfide.

PROPERTIES OF HYDROGEN SULFIDE: a colorless gas with a characteristic unpleasant odor, fairly soluble in water, heavier than air. It burns in an abundance of air to form water and sulfur dioxide, but in a limited supply of air it forms water and sulfur.

The *water solution* is called hydrosulfuric acid; it is a weak acid and forms sulfides with most metallic solutions. Used in chemical analysis to separate metals.

Questions and Problems

1. Describe how you would proceed in the laboratory to prove that a given yellow powder is sulfur.

2. What properties have the allotropic forms of sulfur in common?

3. What other element have we studied which has two allotropic forms? Compare these allotropic forms.

4. Write the names and formulas of four metallic sulfides and of the corresponding oxides.

5. Given that 22.4 liters of air weigh about 29 grams. From the formula of hydrogen sulfide compute its molecular weight and compare its density with that of air.

6. Make a list of the physical properties of hydrogen sulfide.

7. If an aqueous solution of hydrogen sulfide is allowed to stand for some time in a bottle, sulfur is deposited. Explain.

8. How would you recognize a sulfide in the laboratory? An oxide?

9. Write the equations for the following reactions:
(*a*) lead nitrate ($Pb(NO_3)_2$) and hydrogen sulfide;
(*b*) silver nitrate ($AgNO_3$) and hydrogen sulfide;
(*c*) zinc chloride ($ZnCl_2$) and sodium sulfide;
(*d*) copper chloride ($CuCl_2$) and hydrogen sulfide.

10. Write the equations for making silver sulfide in three different ways.

11. If two liters of hydrogen sulfide are burned with an abundance of air, how many liters of sulfur dioxide will be formed? What law is applied here?

12. How many liters of hydrogen sulfide (standard conditions) can be prepared from 500 cc. of hydrochloric acid with an excess of iron sulfide? Assume the hydrochloric acid contains 40% HCl by weight and has a density of 1.2 grams per cubic centimeter.

13. How many grams of iron sulfide are needed to give with dilute sulfuric acid 5 liters of hydrogen sulfide at 15° C. and 60 cm.?

14. Carbon disulfide is burned in air so that 1 liter of carbon dioxide is formed. How many liters of sulfur dioxide are produced?

15. When hydrogen sulfide is passed into zinc sulfate solution, the reaction is reversible. How would you make it complete?

Topic for Further Study

Rubber. When was rubber first used? Why has it become so important during the last twenty years? How can rubber be made synthetically? What is the difference between plantation and native rubber? (Slosson's *Creative Chemistry*, Tilden's *Chemical Discovery and Invention, Chemistry in Industry*, Vol. 1.)

Review Questions

1. Compute the weight of sulfur in 100 grams of chromic sulfate ($Cr_2(SO_4)_3$). Find the result to three significant figures. (Atomic weights: Cr = 52, S = 32, O = 16.)

2. (*a*) What relation exists between the molecular weights and the densities of gases?

(*b*) Arrange the following in the order of decreasing density: CH_4, CO_2, CO, N_2O, NO, NH_3 (Atomic weights: C = 12, N = 14, O = 16, H = 1.)

(*c*) Compute the density of any one of the gases mentioned in (*b*). (One liter of hydrogen weighs 0.09 g.)

3. (*a*) Define an *acid*, a *base*, and a *salt*. (*b*) Write equations illustrating methods for making one member of each of these classes of substances.

4. Write the following equations in complete form, using formulas:

(*a*) (hot) zinc and water (steam)
(*b*) zinc oxide and sulfuric acid
(*c*) magnesium and hydrochloric acid
(*d*) sodium hydroxide and sulfuric acid
(*e*) barium chloride and sodium sulfate

5. What weight of sodium sulfate could be obtained from 10 grams of sodium chloride? (Atomic weights: Na = 23, S = 32, Cl = 35.5, O = 16.)

CHAPTER XVI

OXIDES OF SULFUR AND THEIR ACIDS

Sulfur dioxide — preparation and properties. Sulfurous acid — its uses — sulfites and bisulfites.
Sulfur trioxide — preparation and properties. Manufacture of sulfuric acid — properties of concentrated and dilute — sulfates — test for SO_4 ion.
Acid and basic anhydrides.

Sulfur Dioxide and Sulfurous Acid

178. Preparation of sulfur dioxide. We have already seen that sulfur burns in the air and forms an oxide known as sulfur

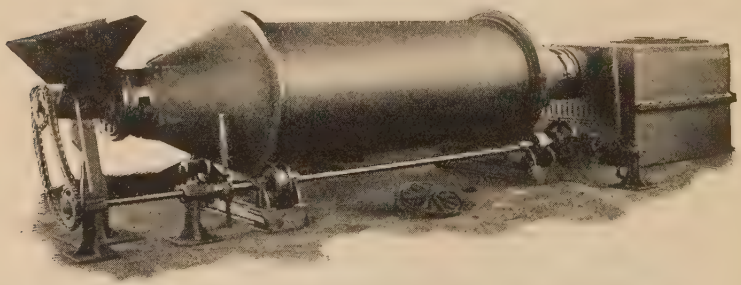


Fig. 97. Rotating drum for burning sulfur to sulfur dioxide.

dioxide (SO_2). This gas has a choking effect familiarly known as " the smell of burning sulfur." The equation is as follows:

$$S + O_2 \longrightarrow SO_2$$

Industrially the sulfur is burned in a rotating drum (Fig. 97). Another method of preparing it consists in heating strongly, or **roasting,** in air a metallic sulfide such as pyrite (FeS_2) or zinc blende (ZnS), which gives the oxide of the metal as well as sulfur dioxide:

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

To prepare sulfur dioxide free from nitrogen and excess of air, we may slowly drop hydrochloric acid on crystals of sodium hydrogen sulfite (Fig. 98):

$$\underset{\text{sodium bisulfite}}{NaHSO_3} + HCl \longrightarrow NaCl + \underset{\text{sulfurous acid}}{H_2SO_3}$$

$$H_2SO_3 \longrightarrow H_2O + SO_2\uparrow$$

This reaction is simply a case of double decomposition, in which one product, the sulfurous acid (H_2SO_3), is unstable and breaks up into water and sulfur dioxide, as shown in the second equation. Another laboratory method consists in heating together concentrated sulfuric acid and copper. The products of this reaction are copper sulfate, water, and sulfur dioxide. The reaction is complicated, but the following equation represents the total change involved:

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow$$

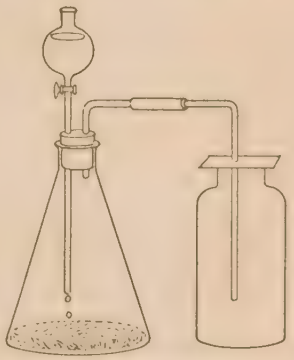


Fig. 98. Preparation of sulfur dioxide.

179. Properties of sulfur dioxide. This gas is colorless but has a characteristic sharp taste and odor. It is more than twice as heavy as air (mol. wt. $SO_2 = 64$; 22.4 liters of air weigh 29 g.), and is one of the most easily liquefied gases known. Under ordinary pressure the liquefied gas boils at $-8°$ C. At room temperatures the liquid may be kept in stout glass bottles or metal cylinders because the pressure is only three or four atmospheres. The gas is very soluble in water, does not burn, and will not support combustion.

180. Sulfurous acid. Sulfur dioxide not only dissolves in water, but also combines with water to form an acid known as sulfurous acid (H_2SO_3). When the water solution is heated, the acid breaks up into water and sulfur dioxide. Thus the reaction is reversible:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

This compound, sulfurous acid, is so unstable that it is impossible to separate it from the water in which it is dissolved. In fact, the main reason why we believe that it exists is that the salts of the acid can be prepared. Thus the acid solution, when neutralized by sodium hydroxide, gives, on evaporation, a substance which corresponds to the formula Na_2SO_3. This would indicate the following equation:

$$\underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{sulfurous acid}}{H_2SO_3} \longrightarrow \underset{\text{sodium sulfite}}{Na_2SO_3} + \underset{\text{water}}{2\,H_2O}$$

Sulfurous acid does not keep; it slowly absorbs oxygen from the air and changes into sulfuric acid. This change is expressed by the equation:

$$\underset{\text{sulfurous acid}}{2\,H_2SO_3} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{sulfuric acid}}{2\,H_2SO_4}$$

On account of the readiness with which it combines with the oxygen from other compounds, sulfurous acid is a powerful **reducing agent.**

For example, potassium permanganate ($KMnO_4$) is a substance very rich in oxygen. We dissolve a crystal in water, getting a deep violet solution. We now pour this colored liquid into some sulfurous acid solution. The result is that the color is *instantly* removed because the sulfurous acid has taken some of the oxygen from the permanganate, leaving colorless compounds in solution.

Fig. 99. Bleaching flowers with sulfur dioxide.

181. Uses of sulfur dioxide. The moist gas (that is, sulfurous acid) is used to bleach straw, silk, and wool — materials which cannot be bleached with chlorine because they become hard and brittle. The bleaching effect disappears after a time, however, and hence materials bleached by sulfur "yellow with age."

This property can be shown by placing a number of moist colored flowers near burning sulfur and then covering the whole with a glass bell jar (Fig. 99). After a short time the flowers become white.

Such foods as dried fruits and canned corn and cherries are sometimes bleached with sulfurous acid. The acid also has antiseptic properties and will prevent the fermentation of sugar, sweet cider, and preserves of various kinds. Its use as a food preservative is, however, questionable. That it is decidedly injurious to plant life is evident from the blighted vegetation in the vicinity of smelters and chemical works where this gas is allowed to escape.

Sulfur dioxide is often used in " iceless " refrigerators. The gas is liquefied by a motor-driven compressor and then is allowed to expand and evaporate. These processes absorb heat and keep the refrigerator cold.

By far the most important use of sulfur dioxide is in the manufacture of sulfuric acid.

182. Sulfites and bisulfites. When sulfurous acid is neutralized by a base, the salt produced is called a **sulfite.** If an excess of sulfur dioxide is passed into the solutions of the bases the acid sulfite, or **bisulfite** ($NaHSO_3$), is formed. Thus:

$NaOH$	$+$	H_2SO_3	$\longrightarrow$	$NaHSO_3$	$+$	H_2O
sodium hydroxide		sulfurous acid		sodium bisulfite		water

In the acid sulfites, or bisulfites, there is one hydrogen atom which has not been replaced, while in the sulfites all the hydrogen atoms have been replaced.

Acids like carbonic acid (H_2CO_3), hydrosulfuric acid (H_2S), sulfurous acid (H_2SO_3), and sulfuric acid (H_2SO_4), which have *two* replaceable hydrogen atoms in each molecule, are called **dibasic acids.** Hydrochloric acid and nitric acid (HNO_3) each have but one replaceable hydrogen atom per molecule and so are **monobasic acids.** Phosphoric acid (H_3PO_4) is a **tribasic acid.** The acid salt may be made by treating the acid with only half enough base to neutralize it, or by adding an excess of acid to the normal salt.

183. Use of bisulfite in making paper. When calcium hydroxide, or slaked lime ($Ca(OH)_2$), is treated with an excess

of sulfurous acid, the product is calcium bisulfite ($Ca(HSO_3)_2$). This reaction is as follows:

$$\underset{\text{calcium hydroxide}}{Ca(OH)_2} + 2\,\underset{\text{sulfurous acid}}{H_2SO_3} \longrightarrow \underset{\text{calcium bisulfite}}{Ca(HSO_3)_2} + 2\,\underset{\text{water}}{H_2O}$$

In making the cheaper varieties of paper, wood is cut into chips and " cooked " with a solution of calcium bisulfite. This dissolves out the objectionable constituent (lignin) of the wood, leaving the pure cellulose, which is the material desired for making paper.

Sulfur Trioxide and Sulfuric Acid

184. Importance of sulfuric acid. In a recent magazine article sulfuric acid was described as the *king of chemicals* because of the fact that there is scarcely an industry in which sulfuric acid is not directly or indirectly used. Why is it so extensively used? For what is it used? How is it manufactured from sulfur?

185. Preparation of sulfur trioxide. It is possible to make sulfur dioxide, when heated, combine with oxygen to a slight extent to form sulfur trioxide (SO_3). But this reaction is exceedingly slow. The rapid combination of sulfur dioxide and oxygen can be effected by the same catalyst that was used for the union of oxygen and hydrogen (§ 41), namely, finely divided platinum. The reaction, which is reversible, is as follows:

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

At about 400° C. nearly all of the two gases unites, but above that temperature the reverse action sets in.

To illustrate this reaction one form of apparatus is shown in figure 100. We first place some platinized asbestos* in a hard-glass tube.

* Clean asbestos is dipped into a rather concentrated solution of platinic chloride and then ignited over the Bunsen flame, leaving finely divided platinum throughout the asbestos.

We burn the sulfur at *S* and draw the mixture of sulfur dioxide and air through the plug *Pt* of the platinized asbestos by means of an aspi-

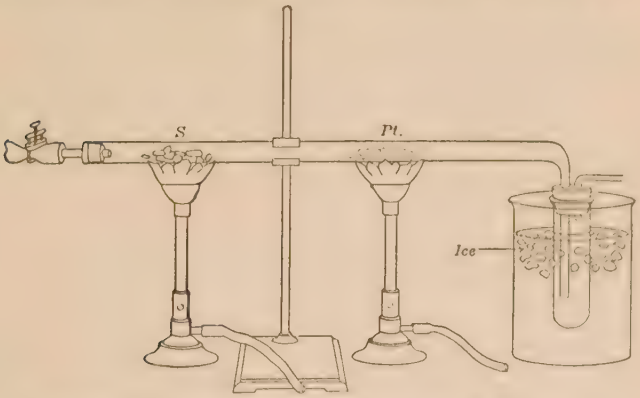


Fig. 100. Making sulfur trioxide by the contact process.

rating arrangement. The plug is gently warmed. The resulting trioxide may be condensed by placing the large test tube in a freezing mixture.

186. Properties of sulfur trioxide. Sulfur trioxide is a colorless liquid which solidifies at about 15° C. and boils at about 46° C. It exists in two allotropic forms; one is the liquid just mentioned, the other is a white crystalline solid which sublimes without melting. Sulfur trioxide combines readily with water, forming sulfuric acid. If the trioxide is thrown into water it dissolves with the evolution of much heat:

$$SO_3 + H_2O \longleftarrow H_2SO_4$$

187. Manufacture of sulfuric acid. Enormous quantities of this acid are manufactured all over the world for use in a great variety of industries. At the present time there are two methods of manufacture: the **contact** process and the **chamber** process. In both processes the first step is the same, namely, burning sulfur or roasting a metallic sulfide to get sulfur dioxide. The chief difficulty comes in the next step; that is, in making

sulfur dioxide into sulfur trioxide. This is overcome by using a **catalyst,** and here is where the principal difference between the two processes lies. In the contact process the catalyst is usually iron oxide which is kept at a definite temperature. In the chamber process the chemical changes are very complicated; the sulfur dioxide is changed to sulfuric acid by the use of steam, oxides of nitrogen, and air. The apparatus is so arranged that the oxides of nitrogen cannot escape and are used over and over again.

In the **contact process** (Fig. 101) the catalytic agent is ferric oxide or, as in our experiment, finely divided platinum. When prepared

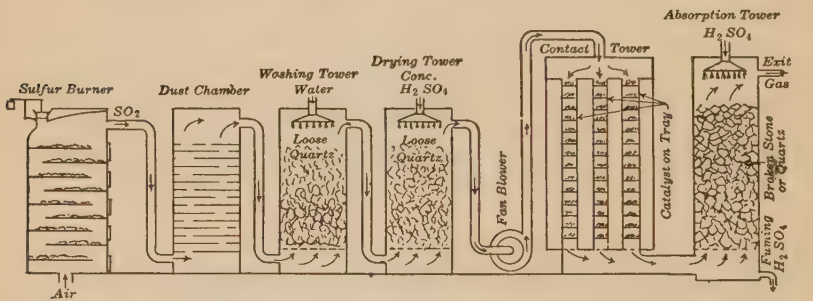


Fig. 101. Diagram of the contact process for making sulfuric acid.

commercially the mixture of sulfur dioxide and air is carefully freed from dust and other impurities; for unless these are removed from the gases the platinum soon loses its catalytic power. The temperature must also be carefully regulated and kept at 400° C.; if it falls below that point the reaction is too slow, and if it rises above it the reverse reaction sets in. Finally, the sulfur trioxide is absorbed in concentrated sulfuric acid (instead of in water) because it has a great tendency to pass through the latter in the form of a mist, or fog, which cannot be caught. The resulting acid is called **fuming sulfuric acid or "oleum";** this is essentially a solution of sulfur trioxide in concentrated sulfuric acid. On dilution with water the sulfur trioxide combines with the water and produces sulfuric acid.

In the **chamber process** (Fig. 102) the oxides of nitrogen are used as the catalytic agent. The sulfur dioxide is oxidized to sulfur trioxide by the aid of nitrogen dioxide (NO_2), a brown gas. The latter sub-

stance (NO_2) is reduced to nitric oxide (NO), but this in turn takes oxygen from the air to form the higher oxide of nitrogen again. Thus the nitric oxide, by being alternately oxidized by the air and reduced by the sulfur dioxide, acts as a carrier of oxygen. The reaction is carried out in large lead chambers. To aid in this process, as well as to furnish the necessary water to convert sulfur trioxide into sulfuric acid, steam is blown into the lead chambers.

In practice the gases from the sulfur or pyrite burners pass through a tower (Glover), which serves to cool the gases and to charge them

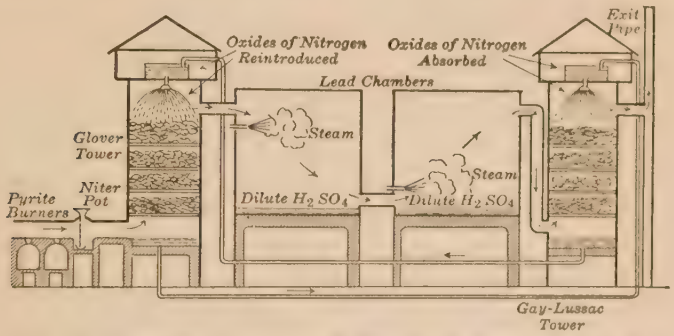


Fig. 102. Diagram of the chamber process for making sulfuric acid.

with oxides of nitrogen. From the last of the series of chambers the gases pass through another tower (Gay-Lussac), in which the oxides of nitrogen are absorbed in concentrated sulfuric acid. This acid is then pumped to the top of the first tower, where it is diluted and gives up the oxides of nitrogen.

The acid which collects in the chambers is only about 60 per cent pure hydrogen sulfate (H_2SO_4). The chamber process is the older method and is still used extensively for making the less concentrated grades of sulfuric acid. For producing concentrated sulfuric acid, the contact process is superior.

188. Properties of concentrated sulfuric acid. Pure sulfuric acid is a colorless, oily liquid about twice as heavy as water. Commercially it is known as **oil of vitriol** because it was formerly made by distilling green vitriol ($FeSO_4 \cdot 7\ H_2O$). It boils at a high temperature (338° C.) and is an exceedingly corrosive substance. If spilled on the skin it produces bad burns. It mixes

with water in all proportions, evolving a large amount of heat. Since the concentrated acid has a great affinity for water it is used for drying many gases.

Closely connected with this avidity for water is the **dehydrating action** of the acid. It will remove hydrogen and oxygen in the form of water from many substances which contain those elements.

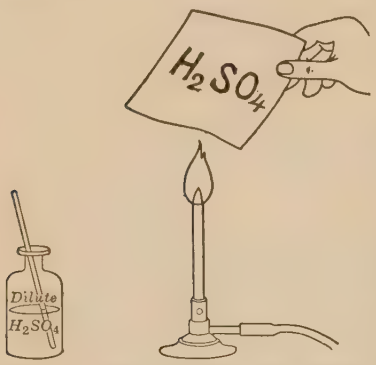


Fig. 103. Charring paper with sulfuric acid.

To show the action of sulfuric acid on paper, which is largely cellulose ($C_6H_{10}O_5$), we may write with a glass rod and some dilute sulfuric acid upon white paper. We dry the paper carefully by holding it at some distance above the Bunsen flame. Where there is writing the paper turns black and charred (Fig. 103) because the dilute acid becomes concentrated through the evaporation of the water.

Hot concentrated sulfuric acid is an **oxidizing agent.** It is reduced to sulfur dioxide and water by many substances. For example, if carbon is boiled in it the carbon is oxidized:

$$2\,H_2SO_4 + C \longrightarrow 2\,SO_2 + 2\,H_2O + CO_2$$

If metals, such as silver, copper, and mercury, are used, they are converted into sulfates; and sulfur dioxide is liberated.

189. Action with salts. On account of its high boiling point, concentrated sulfuric acid is used in **preparing the more volatile acids,** such as hydrochloric and nitric acids. For example, to make hydrochloric acid we use the cheapest **chloride,** common salt:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

The hydrogen chloride is a gas at room temperatures. It will be noted that in the above equation *sodium hydrogen sulfate* ($NaHSO_4$) is one of the products; but if we take twice as much salt and heat

the salt and acid to a higher temperature, we get twice as much hydrochloric acid. This is done on a commercial scale; the equation was given in section 139.

To make nitric acid we use the cheapest of the nitrates, sodium nitrate ($NaNO_3$):

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \uparrow$$

The nitric acid is volatile at 86° C. If we double the quantity of sodium nitrate and heat it to a higher temperature, the nitric acid decomposes; so the actual quantity of nitric acid produced is not doubled.

190. Dilute sulfuric acid. Great care must be taken in diluting sulfuric acid because a large amount of heat is generated. *We pour the concentrated acid in a small stream into the water,* not the water into the acid. It reacts with such metals as zinc, iron, and aluminum, forming free hydrogen and the sulfates of the metal. It can be neutralized with bases, forming salts. Dilute sulfuric acid has no avidity for water, is not an oxidizing agent, and obviously cannot be used for such purposes as preparing hydrogen chloride. In all these respects it differs from the concentrated acid; this distinction should be carefully noted.

191. Sulfates. The salts of sulfuric acid which contain no hydrogen are called **sulfates**; the salts which still have one atom of hydrogen are called **bisulfates** or **acid sulfates.** The sulfates of many metals are very important and are in common use. Thus, **plaster of Paris** is partly hydrated calcium sulfate ($2\,CaSO_4 \cdot H_2O$); **Epsom salt** is hydrated magnesium sulfate ($MgSO_4 \cdot 7\,H_2O$). They are for the most part crystalline solids which are soluble in water. The *sulfates of barium, strontium, calcium, and lead are insoluble.*

The **test for a sulfate,** that is, for the SO_4 radical, is the addition of a soluble barium salt (such as the nitrate) to the solution in question. If a white precipitate is formed which is insoluble in both hydrochloric and nitric acid, a sulfate is present:

$$\underset{\text{barium nitrate}}{Ba(NO_3)_2} + \underset{\text{sodium sulfate}}{Na_2SO_4} \longrightarrow \underset{\text{barium sulfate}}{BaSO_4 \downarrow} + \underset{\text{sodium nitrate}}{2\,NaNO_3}$$

192. Uses of sulfuric acid. Concentrated sulfuric acid is employed as a drying agent both in the laboratory and in the industries. In enormous quantities it enters into the manufacture of dyes and into the production of a number of organic substances which serve as explosives. Because of its high boiling point it is used in the laboratory for the preparation of other acids from their salts. The dilute acid is used in storage batteries and in electroplating; also in cleaning the surfaces of many metals. Large amounts are consumed in the fertilizer industries. It is now one of the cheapest of chemicals (about $10 a ton). On account of its varied and extensive uses, *sulfuric acid may be considered as one of the foundation stones of modern civilization.* (See Industrial Chart, p. 181.)

193. Acid and basic anhydrides. The two oxides of sulfur (SO_2 and SO_3) react with water to produce sulfurous and sulfuric acid respectively. An oxide which combines with water to form an acid is often called an **acid anhydride.** Another example is carbon dioxide, which reacts with water to form carbonic acid (H_2CO_3). Carbonic acid, like sulfurous acid, is unstable and on heating goes back into the anhydride. The reaction is therefore reversible:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

Another acid anhydride is the white oxide obtained by burning phosphorus in air. This combines with water to form phosphoric acid, which like sulfuric acid is stable and does not easily revert to the anhydride:

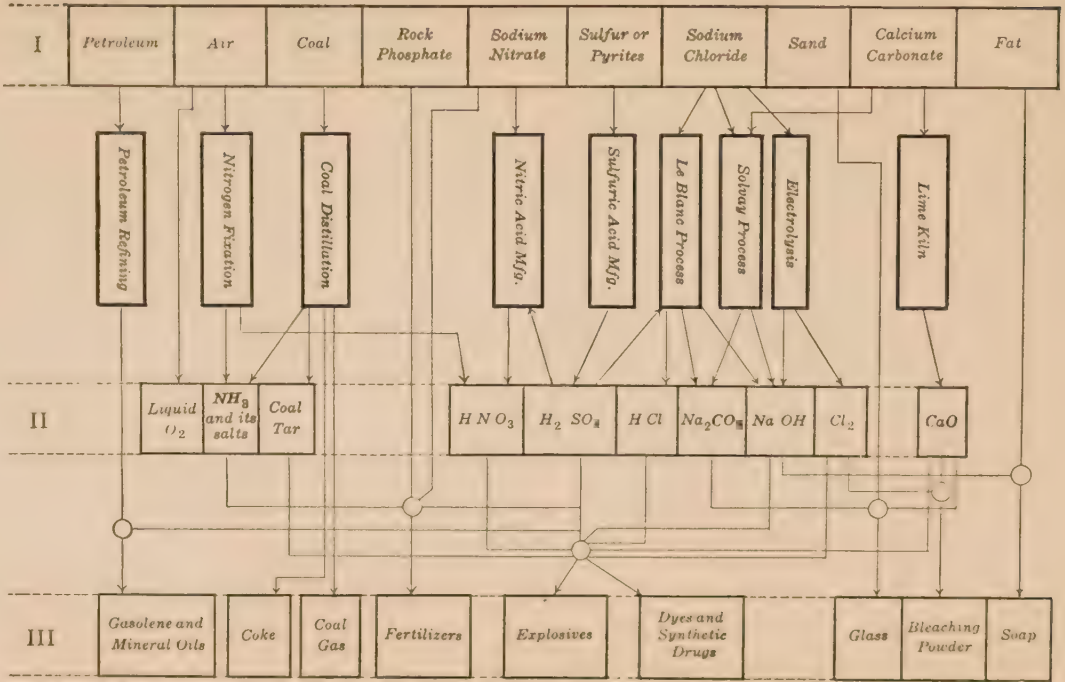
$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4$$

The oxides of such elements as are not metals (and are therefore called **nonmetals**) are acid anhydrides. The oxides of the **metals,** on the other hand, unite with water to form bases. For example, calcium oxide reacts with water to form calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

INDUSTRIAL CHART

Some of the More Important Chemical Processes, Their Raw Materials and Products



Row I Raw materials Row II Chemical products Row III Important familiar materials derived from these raw materials and chemicals

This difference in the behavior of the oxides of the nonmetals and metals is often indicated by calling the former **acidic oxides** and the latter **basic oxides.**

SUMMARY OF CHAPTER XVI

SULFUR DIOXIDE IS PREPARED by:

(1) burning sulfur or by roasting sulfides;

(2) the action of hydrochloric acid on bisulfites;

(3) the action of hot concentrated sulfuric acid on copper.

SULFUR DIOXIDE is a colorless, choking gas which is more than twice as heavy as air. It is very soluble in water.

It is used as a germicide, a preservative, and a bleaching agent. It is also used in certain " iceless " refrigerators. Its main use is in the manufacture of the acids of sulfur.

SULFUROUS ACID is the water solution of sulfur dioxide and is unstable. It is a reducing agent. It has bleaching and antiseptic properties. It forms two classes of salts, *sulfites* and *bisulfites.*

An *acid* which has *two* replaceable hydrogen atoms is called *dibasic.*

SULFUR TRIOXIDE is formed by the union of sulfur dioxide and oxygen with the aid of a catalyst. It unites with water to form sulfuric acid.

SULFURIC ACID IS MANUFACTURED by (1) the *contact* process, in which the sulfur dioxide is oxidized with the help of a catalyst, and (2) the *chamber* process, in which the oxidation is brought about by the use of the oxides of nitrogen.

CONCENTRATED SULFURIC ACID has a strong attraction for water. When hot it is an oxidizing agent. It will drive out other acids from their salts because of its high boiling point.

DILUTE SULFURIC ACID reacts with many metals, forming hydrogen. It forms two classes of salts — sulfates and bisulfates. All sulfates are soluble except those of barium, strontium, calcium, and lead.

SULFURIC ACID IS USED in nearly all industries.

THE OXIDES OF THE NONMETALS, such as SO_2, SO_3, CO_2, P_2O_5, react with water and form *acids.* They are called *acid anhydrides, or acidic oxides.*

THE OXIDES OF THE METALS, like CaO, react with water to form bases; they are called *basic oxides.*

Questions and Problems

1. Write the equation for the reaction when iron pyrite (FeS_2) is roasted and ferric oxide (Fe_2O_3) is one of the products.

2. How many grams of sulfur dioxide can be made by roasting 50 grams of iron pyrite (FeS_2)?

3. How much sulfur will be required to prepare a ton (2000 lb.) of sulfuric acid containing 2% of water?

4. What weight of copper sulfate crystals ($CuSO_4 \cdot 5\,H_2O$) can be made from 100 grams of pure copper?

5. Why does the burning of sulfur in the air not yield *pure* sulfur dioxide?

6. What is an acid anhydride? Give the names and formulas of two anhydrides containing sulfur.

7. Name and give the formulas for the raw materials used in making sulfuric acid.

8. Which is the more stable acid, sulfurous or sulfuric acid? Give your reasons.

9. Explain how sulfurous acid (H_2SO_3) acts as a reducing agent and sulfuric acid (H_2SO_4) as an oxidizing agent.

10. Show how the two oxides of sulfur illustrate the Law of Multiple Proportions.

11. Give two reasons why boiling sulfuric acid causes such serious burns if spilled on the skin.

12. How would you test for a *sulfide*, a *sulfite*, and a *sulfate?*

13. How could you determine whether the sulfuric acid in a bottle were concentrated or dilute?

14. What is the easiest way to bleach a straw hat?

15. Commercial sulfuric acid is generally not colorless. How do you account for the color?

16. What would happen if water were poured *into sulfuric acid?* (Don't try it!)

17. What weight of barium sulfate ($BaSO_4$) is precipitated when a solution containing 26 grams of anhydrous barium chloride is treated with sufficient sulfuric acid?

18. How many liters of sulfur dioxide will be formed by the action of an excess of hydrochloric acid on 54 grams of sodium bisulfite ($NaHSO_3$)?

Topic for Further Study

Catalysis in industry. What would appear to be the advantage of the contact process for producing sulfuric acid over the chamber process? Why has it not entirely superseded the chamber process? What other manufacturing operations use catalysts? What are some of the substances used as catalysts? Duncan's *Chemistry of Commerce, Chemistry in Industry*, vol. 2.

CHAPTER XVII

SOLUTIONS

Importance of solutions. Solvents — saturated solutions — solubility — crystallization — supersaturation — osmosis — boiling points and freezing points of solutions — solutions of gases in liquids — the nature of solutions.

194. Importance of solutions. Not only are solutions very important to the chemist, but they are vitally important to all living things. Our food must be dissolved in the course of di-

Fig. 104. Irrigation has turned this desert region (background) into a fertile fruit-growing region (foreground).

gestion in order to pass into the blood and so be transformed into muscle and bone. Plants take in the nitrogen-containing substances and mineral matter which are in the soil only when

they are in the form of solutions. These enter the roots and are conveyed as sap to the growing parts of the plants.

There are many places in our great West, formerly deserts, which have become fertile simply through irrigation. The addition of water to the land dissolved the food materials which were already in the soil and so made them available as plant food. Figure 104 shows a field before and after irrigation. *No part of the soil can act as plant food unless it is first dissolved.*

The question may be asked, How about "dry farming"? In some arid regions it has been found feasible to prevent the evaporation of the limited amount of moisture by deep plowing and by thorough and constant surface cultivation of the soil. After a time enough moisture may be retained to grow a crop. In certain cases the rainfall is so small that a crop can be grown only once in two years. Dry farming is simply a system of *conserving* the moisture so that the plants may have the amount of water they need to dissolve their food.

195. Solvents. We have seen in Chapter V that water is a very good solvent for many substances. This is particularly true for the compounds known as acids, bases, and salts. There are several other liquids besides water which have considerable solvent power. Alcohol, for example, will dissolve a number of substances, such as shellac, which are not soluble in water. Some substances, like fats, waxes, and gums, are insoluble in water but soluble in certain organic compounds, such as ether, carbon tetrachloride, carbon disulfide, and gasoline. For this reason, when we wish to make a solution of a particular substance, we must try by experiment to find the solvent which is most suitable. This fact is taken advantage of in removing spots from clothing. If the spot is salt or sugar we use water to remove it. If it is a grease spot, however, we use gasoline, carbon tetrachloride (CCl_4), or some similar substance. To remove paint from clothing we must use turpentine or ether, since these are about the only solvents which will dissolve the oily material used in paint.

196. Saturated solutions. There is a certain limit to the amount of material which a solvent will dissolve. This limit varies greatly with the nature of the material to be dissolved and the nature of the solvent. Thus, 100 grams of water at 20° C. will dissolve 34 grams of potassium chloride and only 7 grams of potassium chlorate. When a solution contains a large quantity of the material, it is said to be **concentrated**; when only a small quantity, it is **dilute**; when it contains all the dissolved substance that it possibly can take up at a specified temperature, it is said to be **saturated.** We call the maximum amount of solid which can be dissolved in 100 grams of solvent the **solubility of the substance.** This amount usually varies with the temperature. Solubility curves (Fig. 105) may be drawn by plotting temperatures horizontally and the number of grams dissolved in 100 grams of water vertically. In nearly all cases as the temperature is raised more material can be dissolved. For example, 100 grams of water will dissolve 13 grams of potassium nitrate (KNO_3) at 0° C., 26 grams at 15° C., 169 grams at 80° C.; on the other hand, the solubility of sodium chloride is more constant: 36 grams at 15° C. and 38 grams at 80° C. This difference in solubility is strikingly illustrated in figure 106. A few substances, such as calcium hydroxide ($Ca(OH)_2$), become less soluble as the temperature increases.

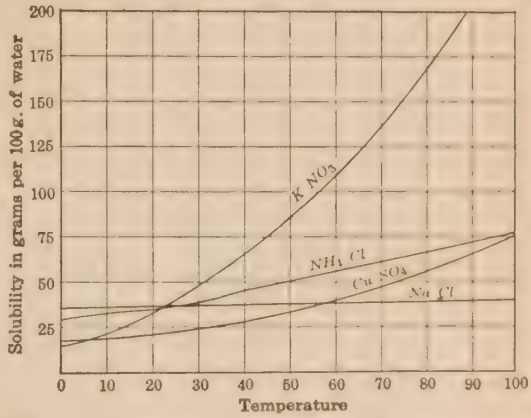


Fig. 105. Curves showing the effect of temperature on solubility.

When the maximum amount of a substance that can be dissolved is very small, we say that the substance is **insoluble.** Strictly speaking, however, no material is absolutely insoluble.

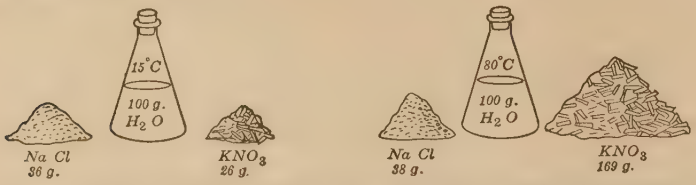


Fig. 106. Relative solubility of salt and saltpeter in cold and hot water.

For example, a saturated solution of powdered marble in water contains 0.00013 grams in 100 grams of water, although we say that marble is insoluble in water.

197. Crystallization. The material which is dissolved in a solution is uniformly distributed throughout the whole solution and is homogeneous to the eye. It will not separate out even on long standing. These are the essential differences between a mechanical mixture like sand and water and a true solution like sugar or salt in water. If some of the solvent is removed by evaporation from a saturated solution, the dissolved material will separate out in the form of crystals. An example of this was given in section 152, where the water evaporated, leaving salt in the form of little cubes. Another way of obtaining a crystalline solid from a solution is to make a saturated solution of the substance at a high temperature and then allow it to cool. If the solubility of the material is much less at the lower temperature, a corresponding amount of solid will separate in the form of crystals. The separation of a solid from a solution in these ways is called **crystallization.**

Crystals can be classified into a small number of classes according to their geometrical form. Examples of some common minerals which occur as crystals are shown in figure 107. The crystalline forms of substances should be observed closely, for they often help to identify the substances.

Fig. 107. Crystals of some common minerals: (1) Gypsum, (2) Galena, (3) Quartz, (4) Barite, and (5) Calcite.

198. Water of crystallization. Some solids take water with them when they separate from a solution. This water seems to be only loosely bound to the rest of the molecule but to be definite in amount. We call it **water of crystallization** and indicate it thus in the formula: $CuSO_4 \cdot 5\ H_2O$ (copper sulfate). Such salts are often called **hydrates,** and the same salt without its water of crystallization is said to be **dehydrated or anhydrous.** For example, crystallized copper sulfate is blue, but dehydrated copper sulfate is white. The water of crystallization can usually be driven off simply by heating the substance; in a few cases it is so loosely held that it is lost even at room temperature. This last process is called **efflorescence.**

There are some salts, such as zinc chloride, magnesium chloride, and calcium chloride, which take moisture from the air on exposure and become wet or even dissolve in the water thus absorbed. Such substances are called **deliquescent.**

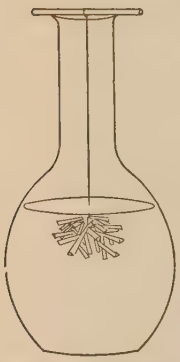


Fig. 108. Crystallization of a supersaturated solution.

199. Supersaturation. Sometimes when we cool a hot, clear, saturated solution to room temperature, no crystals appear even though the solution now contains much more material than could be taken up by the solvent at this temperature. Such a solution is said to be **supersaturated.** Crystals will usually appear in it if it is allowed to stand, or if it is shaken or violently stirred. The addition of a very small crystal of the substance concerned will always bring about crystallization at once.

We may demonstrate this by heating a quantity of sodium thiosulfate, or "hypo" ($Na_2S_2O_3 \cdot 5\ H_2O$), in a clean flask until the salt melts and dissolves in its own water of crystallization. We stopper the flask with cotton batting to keep out the dust and allow it to cool without moving the flask. When it is cold, we suspend in the solution a small crystal of sodium thiosulfate and note the rapid formation of the crystals (Fig. 108).

200. Osmosis. Thin films of vegetable or animal material will allow water to pass readily through them, but completely prevent the passage of many dissolved substances such as cane sugar. If we arrange an apparatus so that a solution is separated from pure water by such a membrane, water passes *into* the solution. This passage of water into a solution through a membrane is called *osmosis*.

By way of illustration we may perform the following experiment. We tie parchment paper over a small glass funnel and make the joint tight with sealing wax; then we fill the funnel with a solution of sugar and attach a long glass tube to the stem by rubber tubing. We place the funnel in a beaker of distilled water, as shown in figure 109. *The solution rises in the tube because of the passing of the water through the parchment.* After several days the solution in the tube will have reached a considerable height.

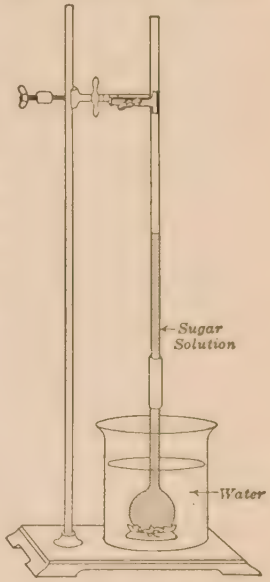


Fig. 109. Apparatus to show osmosis. The water in the beaker passes through the membrane and dilutes the sugar solution.

A membrane which will allow water but not a certain dissolved substance to pass is called a *semi-permeable membrane*. Most vegetable and animal membranes are effective in stopping the passage of sugar but are completely permeable to salt solutions. By precipitating an insoluble copper salt (copper ferrocyanide) in the pores of an earthenware vessel, an artificial membrane may be prepared which is permeable to water but stops even dissolved salts. In living plants and animals, the cells of the tissue are surrounded by membranes which are semi-permeable. Some of these allow nothing but water to go through, others permit the passage of salts but not of other substances like sugar. During the life of a cell its permeability may change, and in this way

the cell regulates its volume and the material which passes into it.

An example of osmosis in living things is the penetration of water and salt solutions into the roots of plants. The water or dilute solution which is taken in by the cells at the root tip is passed from cell to cell farther into the root by osmosis and finally reaches the tubes, or pores, through which it is carried into the stems and leaves. This process continues as long as the cell sap is a more concentrated solution than the soil water. Likewise, the food we eat is changed into liquid form, passes into the blood by osmosis, and is carried throughout the body.

201. Boiling point and freezing point of solutions. Under ordinary conditions pure water freezes at 0° C. and boils at 100° C. *The addition of any soluble solid lowers the freezing point and raises the boiling point.* This lowering of the freezing point is made use of in several ways. For example, the brine which is used in refrigeration plants is a solution of calcium chloride in water. It freezes at a much lower temperature than water and therefore conducts heat away from the water which is to be frozen. Again, if we make a mixture of ice and salt, some of the melting ice forms a saturated solution of salt. A saturated solution of salt freezes at − 21° C., and hence a mixture of ice, solid salt, and a solution of salt can stay together permanently only at this temperature. The result is that more ice will continue melting, thus absorbing heat until the temperature is lowered to − 21° C. A mixture of this kind is called a **freezing mixture** and is used for such purposes as making ice-cream. Since salt water (the sea) freezes at a considerably lower temperature than pure water, it is only in extreme climates that harbors and bays freeze over.

202. Quantitative observations. If we dissolve in 1000 grams of water one gram-molecular weight of sugar ($C_{12}H_{22}O_{11}$), which is 342 grams, and in another liter of water a gram-molecular weight of glycerol ($C_3H_5(OH)_3$), which is 92 grams, we find

that both solutions freeze at the same temperature, namely $-1.86°$ C. We find further that both solutions boil at 100.52° C. In other words, a gram-molecule of any dissolved substance *lowers the freezing point of a given weight of water by a constant amount,* and *raises the boiling point a constant amount.* These experiments indicate that it is not the total weight of material dissolved in a given weight of water that determines the freezing and the boiling points, but rather *the number of molecules in solution.* This fact has furnished another method of determining the molecular weights of many solids and liquids; but we need not describe its details here.

203. Solution of gases in liquids. Thus far we have been considering the solution of solids in liquids; but we shall often have to consider the **solubility of gases in liquids.** It will help us to remember the main facts about the common gases if we divide them into three groups:

1. **Very soluble:** ammonia, hydrogen chloride, and sulfur dioxide.

2. **Fairly soluble:** hydrogen sulfide, chlorine, and carbon dioxide.

3. **Slightly soluble:** oxygen, hydrogen, nitrogen, and the inert gases.

It has been found that an *increase of pressure always increases the quantity of gas going into solution,* and that for slightly soluble gases the increase is directly proportional to the pressure. This is called the Law of Henry, and was formulated in 1803. We have already noted one practical application of it in the manufacture of carbonated water (§ 66).

If we slowly heat a beaker containing cold water, small bubbles of air will be seen to collect in great numbers upon the walls and to rise through the liquid to the surface. It might seem at first that these are bubbles of steam; but they must be bubbles of air, (1) because they are formed at a temperature below the boiling point of water, and (2) because they do not condense as they come to the cooler layers of water above.

This simple experiment shows that ordinary water contains dissolved air, and that the amount of air which water can hold decreases as the temperature rises. *The solubility of gases diminishes with rising temperature.* It is the oxygen of the air that is dissolved in water which supports the life of fish.

204. The nature of solutions. The facts about solutions which we have been considering have led investigators to believe that solutions are in very much the same condition as gases. That is, we think of the molecules of a dissolved substance as moving around among the molecules of the solvent, much as the molecules of a gas fly about according to the kinetic theory. If this conception of solutions is correct, when a substance dissolves in water, it is really separated into individual molecules just as if it were vaporized. We can thus understand why the determining factor in the raising of the boiling point and the lowering of the freezing point is the relative number of dissolved molecules.

Fig. 110. Jacobus Hendricus van't Hoff (1852–1911). Applied the gas laws to solutions; founder of the modern theory of solutions.

If we place a crystal of some colored substance, like copper sulfate ($CuSO_4 \cdot 5\,H_2O$) or potassium permanganate ($KMnO_4$), at the bottom of a tall cylinder of water, we see the color of the material being rapidly distributed throughout the whole solution. This diffusion in a liquid is similar to the way in which one gas diffuses in the presence of another gas.

We have already seen (§ 44) a few drops of bromine (a red liquid) poured into a tall jar of air diffuse upward through the jar. This is a case of diffusion of gases.

These experiments suggest, as we have said, that the structure of solutions may be very much like that of gases. Along these

lines there has been developed in the last 30 years what is practically a **kinetic theory of solutions.** The most striking evidence for the kinetic theory of solutions was worked out by the Dutch chemist van't Hoff (Fig. 110). The theory seems to apply best to dilute solutions; with concentrated solutions it is not so satisfactory. It is probable that in both dilute and concentrated solutions there is some chemical combination between the dissolved substance and the solvent, such as there is known to be in the case of ammonia and water. If this is true, the particles which we imagine are moving around in the solution are not particles of the dissolved substances alone, but are particles of the dissolved substance combined with one or more molecules of the solvent. Some such picture as this represents our present knowledge of solutions.

SUMMARY OF CHAPTER XVII

WATER is the common *solvent* for acids, bases, and salts. Many substances which are insoluble in water will dissolve in alcohol, ether, carbon tetrachloride, or gasoline.

A SATURATED SOLUTION is one which contains in solution all of a given substance which it can acquire. A saturated solution on cooling sometimes becomes *supersaturated.*

SOLUBILITY is expressed as the number of grams of a substance that will dissolve in 100 grams of the solvent. This changes with the *temperature,* usually increasing rapidly with an increase of temperature.

CRYSTALLINE SOLIDS separate from solutions on evaporation, or when a saturated solution is cooled.

WATER OF CRYSTALLIZATION is the definite amount of water with which some substances rather loosely combine when they separate from a solution as crystals.

AN EFFLORESCENT substance loses its water of crystallization at room temperature.

A DELIQUESCENT substance absorbs moisture from the air and dissolves in the moisture.

OSMOSIS is the process by which water passes through a *semi-permeable membrane* which holds back dissolved substances.

Dissolving a substance in a solvent *lowers the freezing point* and *raises the boiling point* in proportion to the *number of molecules* present.

SOLUTIONS are believed to have a *structure much like gases.* The molecules of the dissolved substance move about among the solvent molecules.

Questions and Problems

1. Define and illustrate the meaning of these terms: (*a*) *solvent;* (*b*) *insoluble;* (*c*) *saturated;* (*d*) *dilute solution;* and (*e*) *supersaturated solution.*

2. Compare the freezing point of Great Salt Lake and of Lake Erie.

3. How would you determine experimentally whether a given solution is *unsaturated*, *saturated*, or *supersaturated?*

4. Crystals of washing soda become covered with a coating of white powder. Have they gained or lost weight? Explain.

5. What other substances besides salt might well be used with the ice in an ice-cream freezer?

6. What substances are commonly dissolved in the water of an automobile radiator to lower its freezing point? What are the advantages and disadvantages of each substance?

7. Why is a solution not considered a chemical compound?

8. Why does stirring or shaking make a solid dissolve more rapidly in a liquid?

9. How do you explain the foam on ginger ale after it is opened and poured into a glass?

10. Explain how Henry's Law is applied in the manufacture of "soda water."

11. What is the difference between the action of hydrochloric acid on zinc and the action of water on sugar?

12. What is the percentage of water of crystallization in alum ($KAl(SO_4)_2 \cdot 12\ H_2O$)?

13. How many grams of alum can be made from 276 grams of bauxite ($Al_2O_3 \cdot 2\ H_2O$)?

CHAPTER XVIII

SUSPENSIONS, EMULSIONS, AND COLLOIDAL SOLUTIONS

Suspensions and emulsions — colloidal solutions — the size of colloidal particles — preparation of colloidal solutions — dialysis, ultrafiltration — precipitation — protective action — jellies — dispersions in gases and solids — importance of colloids.

205. Suspensions and emulsions. If we take some very finely powdered substance, such as flour, and stir it up with water, we obtain an apparently uniform mixture. On standing, the solid will slowly settle, and the mixture will thus gradually separate into solid and liquid. Such mixtures are called **suspensions.** Muddy water is a common example of a suspension.

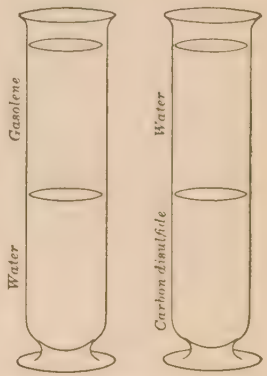


Fig. 111. Immiscible liquids

Many liquids will dissolve in one another in all proportions; for example, alcohol and water. These substances are said to be **miscible** in all proportions. If we mix water and carbon disulfide (CS_2), we very soon notice a sharp line of separation between these two **immiscible** liquids (Fig. 111). Some liquids, such as phenol (C_6H_5OH) and water, have a limited solubility in each other, the solubility depending on the temperature.

If oil and water, two immiscible liquids, are violently shaken up together, small globules of the one may remain suspended in

the other for a long time. This is a mechanical mixture like a suspension, and is called an **emulsion.** Salad dressing is such an emulsion; we make it by shaking up olive oil and vinegar together. Emulsions will separate into the two liquids on standing.

The difference between solutions on the one hand and suspensions and emulsions on the other is probably due to the size of the particles. In a solution we have molecules distributed throughout the liquid which are very small and move about rapidly. In suspensions and emulsions the particles are many thousand times larger than molecules and can be seen with a microscope.

206. Colloidal solutions. Between the true solutions and the suspensions and merging into both we have what are known as colloidal solutions. Many colloidal solutions look perfectly clear when examined with an ordinary microscope; but when a beam of light is thrown through them, they can be seen to be not entirely homogeneous. Thus, if we pass a beam of light through a solution of salt, we see no distinct path. But if we pass a beam of light through a clear colloidal starch solution, we see a bright path (Fig. 112), because the particles in the colloidal solution are large enough to reflect some of the light. A beam of light in a dusty room is visible for much the same reason. If one examines with a microscope the beam of light in a colloidal solution, a multitude of dancing spots of light can be seen. It is not possible to see the tiny colloidal particles themselves, but it is possible to see the points of light reflected by them as they move about in the solution. We can thus count the number of particles in

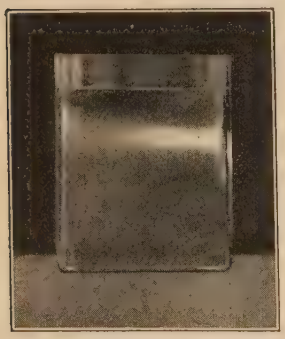


Fig. 112. Light shining through a colloidal solution of starch.

a solution of known concentration and so estimate the size of the particles. An apparatus for doing this is called an **ultramicroscope.**

207. The size of colloidal particles. It has been possible to estimate the size of particles in certain colloidal solutions by means of the ultramicroscope and by other methods. We can compare these values with the direct measurement of suspended

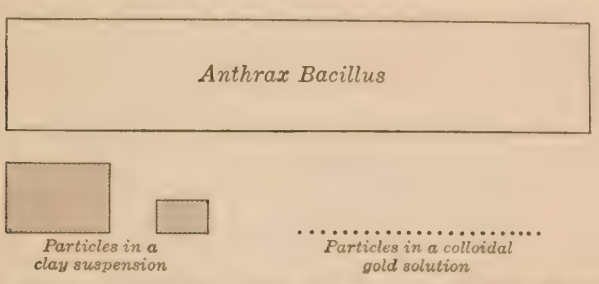


Fig. 113. Diagram showing the relative sizes of bacteria, particles in suspension, and particles in a colloidal solution.

particles (using a microscope) and the calculated size of simple molecules (Fig. 113). Colloidal solutions are those in which the dissolved particles are much larger than simple molecules but still so small that they will not settle out. Matter in this condition is said to be in the **colloidal state** or in colloidal dispersion. Some substances like starch, glue, gelatin, and white of egg always dissolve to give a colloidal solution. This is probably because their complex molecules are so large that they are of colloidal dimensions. Other substances with relatively simple molecules can often be obtained in colloidal solution, in which the particles are aggregates of many molecules (see below). Substances which usually form colloidal solutions are often spoken of as **colloids**; other substances, as **crystalloids.** However, the terms are not exact since many **crystalloids** (*e.g.* gold) may be obtained in colloidal solution, under certain conditions.

208. Brownian movement. If a suspension of very fine particles is examined under a microscope, it will be seen that all the particles are in a state of rapid and irregular motion. The same thing is always noted with the particles made visible in the ultramicroscope. This is called the **Brownian movement** and is characteristic of particles less than about one ten-thousandth of a millimeter in diameter. The irregular and perpetual motion of these tiny particles is due to the fact that they are being bombarded by the molecules of the solvent, which are themselves in constant motion. The Brownian particles serve then to visualize this never-ending dance of the molecules. While we cannot observe the molecules of the solvent, we can see them move and toss around a somewhat larger particle of matter (Fig. 114).

Fig. 114. Path of a Brownian particle as observed under a microscope.

209. Preparation of colloidal solutions. Some substances, such as starch, glue, gelatin, and gum arabic, dissolve in water, forming colloidal solutions. Other substances can be obtained in colloidal solution only by special procedures. For example, colloidal solutions of many metals in water may be prepared by establishing an electric arc between two rods of the metal immersed in water (Fig. 115). The passage of the current mechanically disintegrates the metal into particles which are so small that they stay in colloidal solution. Another method is to prepare the metal by reduction of a solution of the salt; the metal is then produced in a very fine state of division. For example, if a warm gold chloride solution containing sodium carbonate is treated with a few drops of a solution of white phosphorus in ether, the liquid becomes pale

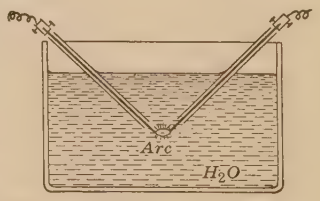


Fig. 115. Making a metallic colloid solution.

yellow, then yellow brown, and finally pure red and perfectly clear. The phosphorus unites with the chlorine, leaving the gold as metallic gold in colloidal solution. Other substances (reducing agents) may be substituted for the phosphorus, and violet or blue solutions may be obtained. The difference in color is due to the difference in the size of the particles. Still another example is the preparation of the red colloidal solutions of antimony sulfide by the action of hydrogen sulfide on an alkaline solution of an antimony salt.

210. Dialysis, ultrafiltration. One of the most striking differences between colloidal particles and simple substances is in regard to the ease of their passage through certain membranes. It is possible to prepare membranes (for example, of collodion) which will allow salts and other substances to pass through but will retain colloids. (The compounds which pass through such membranes were originally called **crystalloids.**) Colloidal solutions may be freed from salts and similar substances by putting them in a collodion bag placed in running water. The crystalloids diffuse into the water, leaving the colloid behind. This process is called **dialysis.** In recent years certain chemists have devised methods of preparing collodion membranes of differing degrees of permeability. Some of these will let certain colloids through but retain others composed of larger particles. This process of **ultrafiltration** is merely an extension of what has long been known about semi-permeable membranes (§ 200). It has proved of great value in purifying colloids and also in estimating the relative size of the particles of different colloids.

211. Precipitation of colloids. Colloidal particles are charged electrically; in some cases all the particles are negatively charged, in others positively. The particles will migrate in an electric field like ions. These charges are usually due to ions which cling to the colloidal particles, that is, are **adsorbed.** If an ion of opposite charge is adsorbed, the charges are neutralized and the neutral colloidal particles usually precipitate. Thus, many colloidal solutions, such as those of the metals and antimony sulfide, are stable only under special conditions. The addition of electrolytes often causes the colloidal particles to clump together and separate as a precipitate (**coagulation**). Usually it is

impossible to cause such precipitates to dissolve again to form a colloidal solution. Thus, if we add acid to the colloidal antimony sulfide solution, a red precipitate of the sulfide forms. Similarly, the addition of any considerable amount of acid or salt to the colloidal gold solution causes the formation of a precipitate of metallic gold.

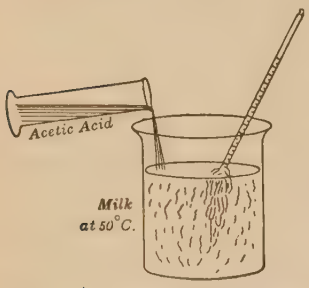


Fig. 116. Coagulation of casein in milk through the addition of acetic acid.

The addition of dilute acetic acid to warm milk causes the precipitation of the colloidal material casein (Fig. 116). In this case the process is said to be reversible, as the casein will dissolve in dilute alkali again, forming a colloidal solution. This same precipitation (coagulation) of casein takes place slowly in the preparation of junket with the aid of rennet, and in making cheese. The crude rubber present in colloidal solution in the sap of rubber trees is also precipitated by the addition of acetic acid; but unlike casein it is not soluble in dilute alkali. It will dissolve in many organic solvents, however, and these solutions are colloidal solutions.

212. Protective colloids. Small amounts of one colloidal substance will often prevent the precipitation of another relatively unstable colloid. Thus, the presence of gum arabic makes easier the preparation of colloidal solutions of metals, as small amounts of salt and acids will no longer cause the formation of a precipitate. **"Argyrol"** is a medicinal form of colloidal silver in the preparation of which some protective colloid is employed.

There are many practical illustrations of the use of protective colloids. The suspension of oil and vinegar, which by itself soon separates, can be turned into a permanent, thick paste—mayonnaise dressing — by the addition of the colloidal material in egg-yolk. The colloidal particles in mayonnaise dressing are little drops of oil, the protective colloid is furnished by the egg. Colloidal solutions in which the dispersed particles are liquids are sometimes called **emulsoids** to distinguish them from the colloidal solutions of solids which are called **suspensoids.**

The protective colloid is also often spoken of as an emulsifying agent. Casein acts as an emulsifying agent in milk, keeping a considerable amount of the butter fat in solution. Colloidal solutions of graphite in water (water dag) or in oil (oil dag) are prepared from finely divided graphite, a solvent, and a protective colloid. They find wide use as lubricants.

Protective colloids probably act because they cling to the other colloid, forming a protecting film. The clinging of one colloid to another or of electrolytes to colloids is called **adsorption.** Finely divided solids or solids with many pores (charcoal) can similarly adsorb large quantities of gases and for this reason were used in **gas masks** during the World War. Charcoal and bone black will adsorb many complex coloring materials from solution and are used in decolorizing solutions in the laboratory and in industry.

213. Jellies. Many colloidal solutions on cooling or on concentration by evaporation turn into jelly-like materials, which are called **gels.** The most familiar example is afforded by the behavior of gelatin, a 5 per cent solution of which sets to a jelly at 18° C. As a rule, on warming or on adding water the gels are transformed into thin liquids (colloidal solutions sometimes called sols). The most remarkable thing about gels is that a very small amount of colloidal material is sufficient to cause the solution to become stiff and rigid. For this reason a relatively small weight of a dry substance like gelatin will in solution produce a large amount of gel. All the fruit jellies that are made directly from the fruit are gels which are produced by the presence of the colloidal substance **pectin** in the fruit. **Solid alcohol** is a gel formed by the action of a saturated calcium acetate solution on denatured alcohol, in the presence of stearic acid.

214. Dispersions in gases and solids. Besides having fine particles dispersed through liquid, we may have a similar state

of affairs in gases and even solids. Smoke is a suspension of very fine particles in a gas (usually air). In some smokes the particles soon unite to form larger masses and settle out, but in other cases the particles stay dispersed throughout the gas for long periods of time. If the suspended particles are those of a liquid we have a fog. A foam is the reverse of a fog, as here fine bubbles of gas are dispersed in a liquid.

Fig. 117. Large smelter *before* installing the Cottrell process.

Smoke particles like other colloidal particles are electrically charged, and Cottrell (an American chemist) has devised a method of precipitating the particles by causing the smoke to move past metal plates and points charged electrically. In the electric field the charged particles move to the electrode, become discharged, and coagulate as a dust. This Cottrell process not only eliminates the "smoke nuisance" connected with many manufacturing operations but enables much precious material otherwise lost to be recovered (Fig. 117). Thus, valuable metallic oxides in the smoke from smelters and foundries, and potassium compounds from cement fumes can be precipitated and used (Fig. 118).

Very fine particles of solid, liquid, or gas may be dispersed throughout a solid mass, and such solid colloidal solutions often have very unusual and beautiful colors. For example, a colloidal solution of gold in glass gives to the glass a ruby-red color. Moreover, only a very small quantity of the colloidal substance is necessary in order to produce a strong color. In the case of the red glass, 0.1 per cent is sufficient.

Fig. 118. Large smelter *after* installing the Cottrell process.

215. Importance of colloidal chemistry. We shall have many occasions throughout this book to refer to the elementary principles of colloidal chemistry just discussed. Plants and animals are composed of complex organic substances which are colloids. The chemistry of plant and animal products and indeed the chemistry of life itself are closely bound up with the phenomena of the colloidal state. The blood, the sap of trees, foods, dyes, rubber, leather, artificial silk — these are just a few examples of colloids and colloidal solutions. Furthermore, colloidal chemistry is of great importance in the industries: the tanning of leather and the manufacture of artificial silk involve a knowledge of colloids.

SUMMARY OF CHAPTER XVIII

SUSPENSIONS are mechanical mixtures of solids and liquids; EMULSIONS are mixtures of liquids and liquids. The particles are large and soon settle.

COLLOIDAL SOLUTIONS contain particles *smaller* than particles in an ordinary suspension and *larger* than the molecules in a true solution. They pass through filters but do not settle. These particles cannot be seen with an ordinary microscope but in many cases reflect light if illuminated with a strong beam.

GLUE, GELATIN, RUBBER, and many other organic substances with large molecules are *natural colloids*. Aggregates of smaller molecules may be prepared by precipitation under special conditions and sometimes by mechanical pulverization.

THE SEPARATION OF SALTS FROM COLLOIDS depends on the fact that colloidal particles do not readily pass through collodion membranes and salts do. By using membranes of different degrees of porosity, different colloids may be separated.

COLLOIDAL PARTICLES ARE ELECTRICALLY CHARGED; if the charge is neutralized by the *adsorption* of an opposite charge, the material precipitates (coagulates). This process may be reversible (casein) or irreversible (gold and rubber).

COLLOIDS can in general be coagulated by adding an *electrolyte*. *Protective colloids* hinder the precipitation of other colloids by electrolytes.

SOLS are liquids which contain dispersed colloids.

GELS are semi-solid mixtures (jellies) which contain colloids that have absorbed some of the suspending liquid.

SMOKES AND FOGS ARE COLLOIDAL DISPERSIONS of solids and liquids in gases. By electrical precipitation smokes may be eliminated and much valuable material recovered.

Questions

1. Define these terms and illustrate their meaning: (*a*) *suspension;* (*b*) *colloidal state;* (*c*) *ultrafiltration;* (*d*) *gel;* (*e*) *dialysis.*

2. Why is it incorrect to say that "one may see and measure colloidal particles with an ultramicroscope"?

3. Do you suppose a colloidal particle of low reflecting power would be visible in the ultramicroscope? Explain.

4. Describe two methods of preparing a colloidal solution of silver. Would it be easier or harder to prepare such a solution if it contained (*a*) gelatin, (*b*) hydrochloric acid? Explain.

5. Rivers contain much colloidal material (clay); explain the deposition of this material in deltas at the river's mouth, where the river water mingles with the ocean.

6. India ink is a mixture of finely divided carbon (lamp black) and some material like gum arabic. What is the function of the gum?

7. How could you most readily determine whether a certain colored solution was colloidal or not?

8. The per cent of iron in hemoglobin (the coloring material of the blood which transports the oxygen) is 0.34. If the molecule contains only one atom of iron, (*a*) what must be its molecular weight? The actual molecule probably contains 4 iron atoms. (*b*) What would be the weight of this molecule?

9. What is meant by the term "adsorption"? Illustrate.

10. In terms of colloidal chemistry explain the "beating of the white of an egg," and the making of "whipped cream."

Topics for Further Study

Household colloids. What common household substances are colloidal gels? How can they be liquefied? What happens when milk stands for some time? Why doesn't the same thing happen to a gelatin solution? (Findlay's *Chemistry in the Service of Man.*)

Glues. Why are glues solutions of colloidal material? What substances have been used in manufacturing glues? What is the relation of glue to gelatin? Why is the latter substance of great importance to the photographic industry? What are some of the uses of casein? (*Chemistry in Industry*, vol. 2.)

CHAPTER XIX

DETERMINATION OF ATOMIC WEIGHTS AND FORMULAS

Why important — standard of atomic weights — approximate atomic weight from molecular weight — combining weights — precise determination of atomic weights — valence by experiment — elements as mixtures, isotopes — finding the formula of a compound.

216. Why atomic weights are important. We have already seen (Chapter XI) that chemical formulas have a quantitative meaning in chemical equations which is of the utmost importance in industrial processes. The precise determination of the atomic weights of the elements is in fact the basis of all our quantitative chemical analysis. Thus far we have shown no experimental evidence to explain why a molecule of water is represented by H_2O, a molecule of sulfuric acid by H_2SO_4, and a molecule of acetylene gas by C_2H_2. In this chapter we shall discuss *first*, how the atomic weights of the elements are determined by experiment, and *second*, how these atomic weights are used to find the formula of a compound.

217. Atomic weights by direct comparison. Another result of Avogadro's principle is that it gives us a direct method of calculating the relative weights of the atoms, that is, the atomic weights. We have seen that the oxygen molecule is approximately 16 times as heavy as the hydrogen molecule, and we have also seen that the oxygen and hydrogen molecules each have 2 atoms. Therefore we can say that the oxygen atom is about 16 times as heavy as the hydrogen atom. Since the atomic

weight of oxygen is taken as 16 and is our standard, the atomic weight of hydrogen is 1.008.

In the same way we can compute the atomic weight of nitrogen as 14 and of chlorine as 35.5. We determine the weight of 22.4 liters and, knowing that each of these molecules contains two atoms, take half the molecular weight thus determined. Unfortunately we cannot apply this same method to all the elements because we cannot obtain them in the gaseous condition.

218. Atomic weight from molecular weight. We have seen that the molecular weight of a substance expresses the weight of its molecule compared with the oxygen molecule as 32; and that the atomic weight of a substance expresses the weight of its atom compared with the oxygen atom as 16. Since the oxygen molecule contains two atoms, *the basic unit for both molecular and atomic weights is the oxygen atom taken as 16.* It has also been pointed out that the molecular weight of a compound is equal to the sum of the atomic weights of its constituent atoms.

It is possible (by means of its density if it is a gas, and also by other methods not described here) to determine experimentally the molecular weight of a compound; it is also possible to determine experimentally its percentage composition by weight. We can then find the weight of the element in the molecular weight by multiplying the molecular weight by the per cent of the element. Further, if we analyze several compounds of the same element, we shall find that the numbers obtained by multiplying the molecular weights by the per cent of the element will in each case be the same, or multiples. We then take as the atomic weight the smallest weight of the given element in the compounds considered. In other words, by this method *the smallest weight of an element found in the gram-molecular weights of its compounds is the atomic weight of that element.*

For example, let us determine the atomic weight of the element carbon. This element forms a number of gaseous compounds, whose molecular weights can easily be determined by finding their densities (grams per liter) and multiplying by 22.4 (§ 162). The molecular weights of four such gaseous compounds of carbon (carbon dioxide, carbon monoxide, marsh gas, acetylene) are given in the following table. We determine by experiment the percentage of carbon in each of these gases; the results are given in the third column. If we now, in each case, multiply the molecular weight by the percentage of carbon, we shall find what part of the molecular weight is due to the carbon (fourth column).

Name of Gas	Molecular Weight (22.4 l.)	Percentage of Carbon by Experiment	Part of Molecular Weight due to Carbon
Carbon dioxide . . .	44.28	27.27	12.08
Carbon monoxide . . .	28.02	42.86	12.01
Marsh gas	16.06	75.0	12.08
Acetylene	25.98	92.31	23.98

From the results in the fourth column it is evident that "the smallest weight of this element found in the gram-molecular weight of its compounds" is about 12. Therefore *the atomic weight of carbon is approximately 12.* No compound has ever been found which gives a smaller weight for carbon.

Problems

1. Calculate the atomic weight of sulfur from the following data about some sulfur compounds:

Compounds	Molecular Weight (22.4 l.)	Percentage of Sulfur
Hydrogen sulfide	34.08	94.06
Sulfur trioxide	80.06	40.04
Sulfur monochloride	135.04	47.48
Carbon bisulfide	76.12	84.24
"Mustard gas"	158.98	20.16

2. Determine the atomic weight of nitrogen from the following data about nitrogen and its compounds:

Name of Gas	Density (Grams per Liter)	Percentage of Nitrogen
Nitrogen	1.251	100.0
Nitrous oxide	1.978	63.7
Nitric oxide	1.340	46.7
Ammonia	0.771	82.3
Cyanogen	2.33	53.8

219. Atomic weights and combining weights. If we analyze hydrogen chloride we shall find that 35.46 grams of chlorine are united with 1.008 grams of hydrogen. The chemist calls this number 35.46, the **combining weight** or **reacting weight** of chlorine. *The* ***combining, or reacting, weight*** *of an element is the weight of that element which combines with or replaces 1.008 grams of hydrogen.* It will be seen at once that this combining weight is equal to the atomic weight of chlorine, which we have already determined by comparing the densities of the elementary gases chlorine and hydrogen. Indeed, this combining weight *must* be its atomic weight, because a molecule of hydrogen chloride (HCl) consists of but one atom of hydrogen combined with one atom of chlorine.

Unfortunately the combining weights of some elements are *not* equal to their atomic weights. If we analyze water (§ 55) we find that 1.008 parts of hydrogen unite with 8 parts by weight of oxygen, and therefore the combining weight of oxygen is 8, or *one-half its atomic weight.* This is because one atom of oxygen (16) unites with two atoms of hydrogen (2.016) to form water. It has been found in general that *the atomic weight of an element is equal to its combining weight or some multiple of it.* In the case of oxygen this multiple is 2.

Let us take the case of an element which does not combine with hydrogen but which replaces it. Such an element is sodium; its combining weight may be determined as follows:

If we put metallic sodium in water, hydrogen and sodium hydroxide are formed. When this experiment is done quantitatively, we find that 23.00 grams of sodium replace 1.008 grams of hydrogen. Therefore the combining weight of sodium is 23.00.

220. How to determine the combining weight. The question might easily arise, How can we determine the combining weight of an element which does not combine with or replace hydrogen? If we analyze black copper oxide, we find that 31.8 grams of copper are combined with 8.00 grams of oxygen. That is, the combining weight of oxygen (8.00 grams) is united with 31.8 grams of copper; hence we feel sure that if copper and hydrogen did unite, 31.8 grams of copper would combine with 1.008 grams of hydrogen. The combining weight of copper is therefore 31.8.

In general, *when an element does not unite with or replace hydrogen, we can determine its combining (or reacting) weight by finding the weight of it which will unite with the known combining weight of another element.*

221. Precise determination of atomic weights. The combining, or reacting, weight of an element can be determined in the laboratory with great accuracy. A method for determining atomic weights has already been described which involves finding the density of gas (§ 217). This is difficult to do with exactness. To find the precise atomic weight of an element, we determine the combining, or reacting, weight with great care and then multiply by some small whole number which will make the result agree with the approximate value. For many reasons chemists have found it convenient to call the *atomic weight of oxygen exactly 16.00*, which makes the atomic weight of hydrogen 1.008.

These values for atomic weights are thus, obviously, dependent on the precise chemical analysis of compounds. Such experimental work must be done with extreme care and extraordinary precision. One of the first chemists to make a systematic study of atomic weights was

Berzelius. His methods have been greatly improved upon by later chemists, and to-day the accepted atomic weights are the result of very elaborate experiments. Theodore W. Richards (Fig. 119) is the foremost modern chemist in this field of investigation.

Fig. 119. Theodore William Richards (1868–). Professor of chemistry at Harvard University. Received Nobel prize for his work on atomic weights.

222. Summary of the steps in an atomic weight determination. We may now restate the necessary steps in determining the atomic weight of an element.

First, Find the approximate atomic weight. To do this, (*a*) determine the molecular weights of a number of gaseous compounds by finding their densities; (*b*) determine the percentage of the element in each of these compounds by carefully analyzing them; (*c*) find what part of the molecular weight is due to the element by multiplying the molecular weight of the compound by the percentage of the element in it; (*d*) note the smallest weight of the element which is found in the gram-molecular weight of these compounds.

Second, Determine very accurately the combining weight of the element in one or more compounds.

Third, Multiply the combining weight by some small whole number (1, 2, or 3) which will give a result close to the approximate atomic weight. The number thus obtained will be the *precise atomic weight.*

223. Valence by experiment. We have just learned that the atomic weight of an element is either identical with or some

multiple of its combining weight. *That factor by which we multiply the combining weight in order to get the atomic weight is the valence.* For example, the combining weight of zinc is 32.7, and its atomic weight is 65.4. The valence of zinc is two. Again, the combining weight of aluminum is 9.00, its atomic weight is 27.0, and its valence is three. In other words,

Atomic weight = combining weight × valence

224. Elements as mixtures. Isotopes. We have assumed throughout this discussion that all the atoms of an element were alike. This was long thought to be the case but is now known to be untrue. Many elements are composed of several different kinds of atoms which differ only in the relative mass of the atoms. Our atomic weights of these elements are therefore averages. The different kinds of a given element are called **isotopes.** These isotopes are identical in all chemical reactions, and for practical purposes the element behaves as though it were homogeneous. The evidence for the existence of isotopes first came from a study of radioactive substances (§ 520), and later a physicist Aston invented a method of comparing the masses of individual atoms, thus discovering isotopes of many common elements. For example, chlorine with an atomic weight of 35.46 was found to be a mixture of two isotopes of atomic weights 35 and 37. The following table gives a short list of elements and their isotopes according to Aston:

Element	Atomic Weight	Minimum Number of Isotopes	Atomic Weight of Isotopes in Order of Intensity
Lithium	6.94	2	7, 6
Boron	10.8	2	11, 10
Neon	20.2	2	20, 22
Chlorine	35.46	2	35, 37
Bromine	79.92	2	79, 81

It will be noted that the atomic weights of the individual isotopes are very nearly whole numbers. The significance of

this fact will be explained later (§ 523). As yet we do not know of isotopes of hydrogen, helium, carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur, and arsenic. This indicates that these are simple elements.

225. Determining the formula of a compound. To find the precise value of atomic weights requires very great technical skill and patience. *For most of us the important thing is to learn to use atomic weights.*

One very important use of atomic weights is in finding the formula of a compound. We shall now illustrate this by determining the formulas of water, sulfuric acid, and acetylene.

Water. We find that its percentage composition is as follows: hydrogen 11.19 per cent, and oxygen 88.81 per cent. By experiment we also find that its molecular weight is approximately 18. Then the solution is as follows:

	Percentage composition		Atomic weight		Atomic ratio
Hydrogen . . .	11.19	÷	1	=	11.2
Oxygen	88.81	÷	16	=	5.55

Dividing the percentages (by weight) by the atomic weights gives as quotients numbers which show the relative number of each kind of atom. If we assume that there is one atom of oxygen in the molecule, then there must be 2 atoms of hydrogen. In other words, divide the several quotients in column three by the smallest one of them. (That is, $11.2 \div 5.55 = 2$.) Therefore the simplest formula for water is H_2O. This gives a molecular weight of $2 + 16$ or 18, which corresponds with the experimental value given.

Sulfuric Acid. Given the percentage composition: hydrogen 2.04 per cent, sulfur 32.65 per cent, and oxygen 65.31 per cent.

	Percentage composition		Atomic weight		Atomic ratio
Hydrogen	2.04	÷	1	=	2.04
Sulfur	32.65	÷	32	=	1.02
Oxygen	65.31	÷	16	=	4.08

These quotients are evidently in the same ratio as the number of atoms of each element in the molecule. That is, there are 2 atoms of hydrogen (2.04 ÷ 1.02), 1 atom of sulfur (1.02 ÷ 1.02), and 4 atoms of oxygen (4.08 ÷ 1.02); and the simplest formula of sulfuric acid is H_2SO_4. In this case the molecular weight is very difficult to obtain, and so we accept the simplest formula.

Acetylene. Suppose we have given that the gram-molecular weight of acetylene is 25.98, that it contains 92.31 per cent carbon, and that the rest is hydrogen. To find the formula of acetylene the solution may be arranged thus:

	Percentage composition		Atomic weight		Atomic ratio
Carbon	92.3	÷	12	=	7.7
Hydrogen	7.7	÷	1	=	7.7

The simplest formula would be CH, but then the molecular weight of CH would be 13. Hence, in order to get the experimental value 25.98, the formula must be *doubled*. Therefore the formula for acetylene is C_2H_2.

Problems

1. A certain gas contains 30.4% nitrogen and 69.6% oxygen. What is the simplest formula which could be used to express its composition?

2. The analysis of a certain compound showed: hydrogen 0.84%; carbon 10.05%; and chlorine 89.11%. What would be the simplest formula which represents this composition?

3. A certain carbon compound contains by weight: carbon 52.18%; hydrogen, 13.04%; oxygen 34.78%. What is its simplest formula?

4. Determine the simplest formula for an ore that has the following analysis: uranium 84.82%; oxygen 15.17%.

5. The composition of a copper ore is as follows: copper 79.45%; sulfur 20.32%. What is the simplest formula?

6. The analysis of a substance showed carbon 80% and hydrogen 20%. The molecular weight was found to be 30. What is its formula?

7. A gas by analysis was found to have the following composition: carbon 73.8%; hydrogen 8.7%; and nitrogen 17.5%. Its molecular weight was found to be 160.4. Find the formula of this compound.

8. A certain compound is found to contain carbon 92.3% and hydrogen 7.7%, and 1.10 grams of its vapor is found to occupy 314 cc. under standard conditions. What is its formula?

9. The analysis of ammonia gas shows that it is 82.4% nitrogen and that the remainder is hydrogen. Compute the combining weight of nitrogen.

10. From a study of the following data in regard to nitrogen compounds and from the combining weights found in the previous problem calculate (*a*) the atomic weight of nitrogen, and (*b*) its valence:

Nitrogen Compounds	Density (Grams per Liter)	Per Cent of Nitrogen
Ammonia	0.762	82.4
Nitrous oxide	1.97	63.6
Nitric oxide	1.34	46.7

11. To determine the molecular weight of the compound used in Problem 2, an experiment was performed which showed that 0.250 g. of the substance gave 53.0 cc. of gas when collected over water at 20° C. and 740 mm. Calculate the gram-molecular weight of the substance, and revise your answer in Problem 2 accordingly.

12. The compound used in Problem 3 was heated to 150° C., and it was found that 185 cc. of the gas formed weighed 0.247 grams. (*a*) What was its gram-molecular weight? (*b*) What is the formula of the compound?

SUMMARY OF CHAPTER XIX

ATOMIC WEIGHT of an element is a number which expresses the relative heaviness of its atom. Atomic weight of oxygen, 16, is taken as the standard.

Atomic weight of an element *is determined* approximately by getting the number representing the smallest weight of the element in the gram-molecular weight of any of its compounds.

COMBINING, OR REACTING, WEIGHT of an element is the weight of that element in grams which combines with or replaces 1 gram (more exactly 1.008 grams) of hydrogen.

ATOMIC WEIGHT is either equal to or a multiple of the *combining weight.*

ATOMIC WEIGHT = combining weight × valence.

ISOTOPES are forms of the same element which differ slightly in atomic weight but are alike in chemical behavior.

TO FIND THE FORMULA FROM PERCENTAGE COMPOSITION: Divide the percentage of each element by its atomic weight; the quotients will be the relative number of each kind of atom. Use molecular weight to find what multiple of the simplest formula to use.

Questions

1. What is the distinction between atomic weights and molecular weights?

2. In what cases is the atomic weight equal to the molecular weights?

3. What is the distinction between atomic weights and combining weights?

4. In what cases is the atomic weight equal to the combining weight?

5. Sometimes the combining weight is referred to as the equivalent weight. Explain the significance of "equivalent" in this use.

6. Show how Avogadro's principle furnishes the basis for the determination (*a*) of molecular weights and (*b*) of atomic weights.

7. Why was the oxygen atom chosen as the standard for atomic weights instead of the hydrogen atom?

8. Why can a chemist determine the combining weight of an element with more precision than the molecular weight of a gas?

9. Why should the table of precise atomic weights need to be revised from time to time?

10. Why was it so difficult for chemists to find the isotopes of which such elements as chlorine are made up?

Topic for Further Study

The precise determination of atomic weights. The modern methods of atomic weight determination involve many experimental precautions; the fundamental chemical facts are, however, very simple. Consult the work of Morley on hydrogen and oxygen (Smithsonian Contributions, No. 980) and Richards on chlorine and silver (Carnegie Publication, No. 69).

CHAPTER XX

AMMONIA AND AMMONIUM COMPOUNDS EQUILIBRIUM

Household ammonia — composition and formula — preparation — properties — refrigeration — ammonium hydroxide and ammonium salts — commercial uses — manufacture of ammonia from coal and synthetically from elements.

Claude's process of fixation of nitrogen — reversible reactions — kinetic equilibrium — effect of catalysts. Effect of temperature and other conditions on the rate of a reaction. Law of Mass Action.

226. Household ammonia. The cleansing agent which is commonly used in the household is labeled **ammonia** or, more accurately, **ammonia water.** The name "ammonia" properly belongs to the gas which causes the familiar, peculiarly pungent smell of the cleanser. This gas is extremely soluble in water and is therefore usually sold in water solution. It owes its cleansing qualities to the fact that it is a base. Since both ammonia gas and water are volatile, it was formerly called the "volatile alkali."

227. Composition of ammonia. When we heat ammonia water, we get a gas which can be shown to be composed of nitrogen and hydrogen. To demonstrate the fact that ammonia contains nitrogen, we lead the dried gas through a tube containing hot copper oxide. We find that the copper oxide is reduced to metallic copper, water is formed, and a gas comes from the delivery tube, which proves to be **nitrogen.** The presence of hydrogen in ammonia might be inferred from the formation of water in this experiment, a compound of hydrogen and oxy-

gen. But we can definitely prove that it is a constituent of ammonia by passing the gas through a tube containing heated magnesium. In this case the gas set free is **hydrogen.** The product left in the tube is magnesium nitride (Mg_3N_2), which when put in water gives us ammonia again.

To determine the formula for ammonia we have only to perform the experiment with copper oxide in a quantitative way. The results of such experiments show that ammonia is 82.3 per cent nitrogen and 17.7 per cent hydrogen. Dividing the percentages by the respective atomic weights, we get the ratio of the atoms to be *one* of nitrogen to *three* of hydrogen. Since one liter of ammonia weighs about 0.77 grams, the gram-molecular weight (that is, the weight of 22.4 liters) is 17.2. This corresponds to a formula NH_3.

We may write the equations for these reactions:

$$3\,CuO + 2\,NH_3 \longrightarrow 3\,Cu + 3\,H_2O + N_2$$
$$3\,Mg + 2\,NH_3 \longrightarrow Mg_3N_2 + 3\,H_2$$
$$Mg_3N_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,NH_3$$

228. Laboratory preparation of ammonia. By heating a water solution of ammonia we can conveniently prepare the pure gas. When the solution is boiled, the dissolved gas is expelled because it is much less soluble in hot than in cold water. If we wish to free the gas of water vapor, we arrange the apparatus (Fig. 120) so that the ammonia passes up through a **drying tower** which is filled with pieces of soda lime (NaOH and CaO). Because of its extreme solubility in water, the gas is collected in a bottle held mouth down, from which it displaces the air.

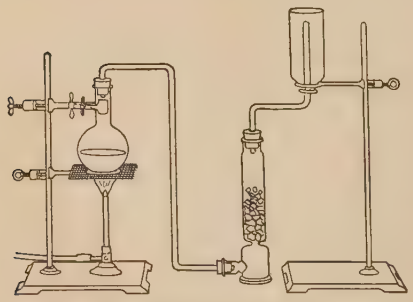


Fig. 120. Preparation of dry ammonia.

Another convenient way of preparing the gas is by heating a mixture of ammonium chloride, or sal ammoniac (NH_4Cl), and slaked lime ($Ca(OH)_2$) in a large test tube, as shown in figure 121. The reaction is as follows:

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\,H_2O + 2\,NH_3\uparrow$$

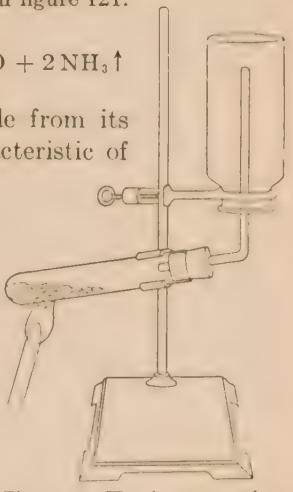


Fig. 121. Heating ammonium chloride and lime.

229. Properties of ammonia. Aside from its pungent odor the most striking characteristic of ammonia is its extreme solubility. It is even more soluble in water than hydrogen chloride.

The rapidity with which ammonia gas is absorbed by water may be shown by the following experiment. A large flask is entirely filled with ammonia, and a stopper is inserted through which runs a long tube and a "dropper" containing water. The lower end of the tube dips into a beaker which contains a red litmus solution (slightly acid). By pinching the rubber bulb a little water is ejected into the flask, whereupon the contents of the beaker at once rush up into the flask (Fig. 122), and the *red solution becomes blue.*

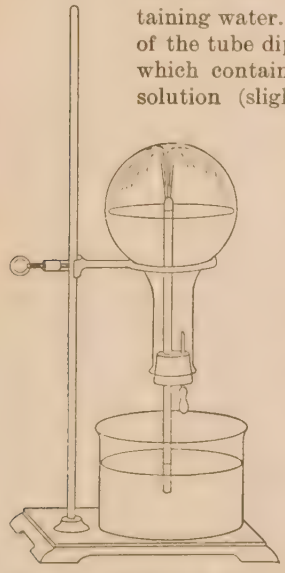


Fig. 122. Ammonia is extremely soluble in water.

As might be supposed from its molecular weight 17, ammonia is about one-half as heavy as air. It is easily liquefied; at ordinary temperatures a pressure of only about 9 atmospheres (132 pounds per square inch) is needed.

230. Refrigeration with liquid ammonia. Liquid ammonia is very extensively used in making artificial ice and in producing the low temperature

required in cold-storage plants. This use of ammonia depends on the fact that it can easily be liquefied at ordinary temperatures by applying pressure, and that when this pressure is released, the gas evaporates, absorbing a great deal of heat from the surroundings.

Figure 123 shows how this principle is applied in the production of artificial ice. The gas is compressed by pump *A* and is forced through the coil of pipe, where the heat produced by the compression is removed by running water. When the ammonia emerges from this coil, it is at room temperature and under sufficient pressure to be a liquid. The liquid ammonia flows through an expansion valve, which connects with the long series of coils; these are made of large pipe and are under atmospheric pressure. In these pipes the liquid now evaporates (because it is under atmospheric pressure), and in so doing it absorbs heat from the surrounding bath of brine. The gas is returned to the pump and again makes the cycle. The temperature of the brine is thus lowered to about $-15°$ C. The brine, which is a solution of common salt or calcium chloride ($CaCl_2$), does not freeze at this temperature. Pure water in suitable metal containers is immersed in it and is frozen in from 24 to 36 hours into cakes of ice (Fig. 124). The usual form of "iceless" refrigerator works on the same principle, except that sulfur dioxide is used more commonly than ammonia.

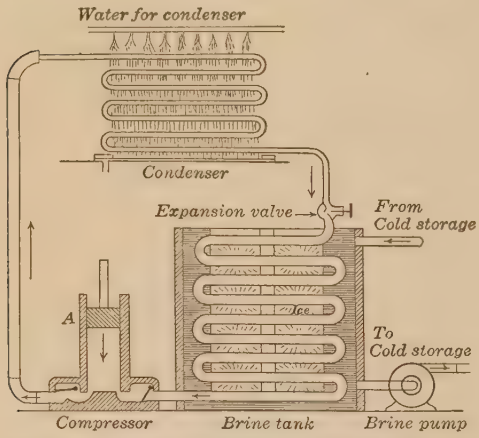


Fig. 123. Diagram to show the principle of a refrigeration plant.

If it is desired to keep the interior of a room at a low temperature, the brine itself is circulated by means of a pump through coils of pipe placed in the room; it then returns to the tanks

containing the ammonia coils. The temperature of a room can thus be kept very low, and meat and other food placed in it can be preserved for a long time, since at this low temperature decay and putrefaction practically cease (Fig. 125).

Fig. 124. Lifting the cakes of ice formed artificially.

In many cities the entire ice supply is produced in plants using the ammonia process just outlined. Cold-storage plants which are cooled by ammonia refrigeration machines are located wherever convenient, in connection with the handling of food products. Thus, many hotels and clubs have small ammonia refrigeration plants.

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Fig. 125. Inside view of a refrigeration room.

231. Ammonium hydroxide. The action of ammonia upon water does not seem to be merely a solution of the gas in water, since the resulting solution has basic properties. It turns red litmus blue; it feels soapy and slippery to

the touch; it neutralizes acids, forming salts. Therefore it appears as though a part of the gas must combine chemically with water as indicated in the equation:

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

The product of the reaction is called **ammonium hydroxide.** When this solution is heated, the compound decomposes into ammonia and water. Therefore the equation is written to represent a reversible reaction.

232. Ammonium salts. When ammonia and hydrogen chloride combine at ordinary temperatures, the product is a white crystalline solid called ammonium chloride (NH_4Cl):

$$NH_3 + HCl \longrightarrow NH_4Cl$$

This reaction can be shown very prettily by taking two clay pipes and moistening the inside of one with a concentrated water solution of ammonia and the other with concentrated hydrochloric acid. When the mouths of the two pipes are brought near each other, a white cloud of ammonium chloride particles is produced (Fig. 126). Enough of the gaseous ammonia and gaseous hydrogen chloride escape from the aqueous solution to cause this reaction to take place in the air surrounding the pipes.

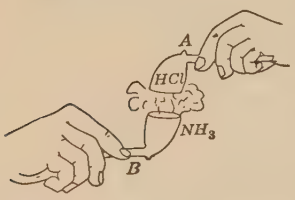

Fig. 126. Union of ammonia with hydrogen chloride.

When ammonium hydroxide is neutralized with hydrochloric acid and the solution is evaporated to dryness, a white solid results which is identical with that produced by the union of gaseous ammonia and hydrogen chloride. This is, of course, **ammonium chloride,** or **sal ammoniac:**

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

Although the ammonium radical (NH_4) has never been obtained in a free state, yet we have many ammonium salts. In

all of these compounds this group of atoms NH_4 acts very much like a monovalent metal, such as potassium or sodium.

When ammonium salts are heated in a dry tube, they are decomposed and most of them give ammonia and an acid. For example,

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

It will be noticed that in this case both products are volatile, but when these products are cooled, they reunite to form the solid ammonium chloride. Here again we have a case of a reversible reaction.

In order to liberate ammonia from its salts, we have merely to heat any ammonium compound with an alkali (such as lime or sodium hydroxide) in order to neutralize the acid; we then get the unmistakable odor of free ammonia. This can be used as a **test for ammonium salts.**

233. Uses of ammonia. We have already seen that liquefied ammonia is used for refrigeration purposes, being shipped in strong steel cylinders. Large amounts of it are used in the new method of preparing nitric acid (§ 244). The aqueous solution, **aqua ammonia,** is used as a cleanser both in the home and in the industries. Ammonium sulfate ($(NH_4)_2SO_4$) is a valuable fertilizer since it contains a large percentage of nitrogen and, like all ammonium salts, is very soluble. Sal ammoniac (NH_4Cl) is used commercially in the manufacture of several types of cells. Ammonium nitrate (NH_4NO_3) is used in explosives because it decomposes easily and leaves no solid products.

234. The manufacture of ammonia. Ammonia was formerly produced entirely from the liquor obtained as a by-product in the distillation of coal (§ 346). Now increasing amounts are being prepared synthetically, that is, by the direct combination of the elements. The ammonia thus prepared is used for the purposes described above and in particular for the production of nitric acid and nitrates (§ 244).

235. Nitrogen fixation. It has long been known that if electric sparks are passed through a mixture of nitrogen and hydrogen, a small amount of ammonia can be produced by synthesis from the two elements. Two processes have been developed for combining these gases on an industrial basis. In both processes a mixture of nitrogen and hydrogen under pressure is heated to about 500° C., and then passed over especially prepared iron finely divided, which acts as a catalyst. In the original **Haber process** a pressure of 200 atmospheres is used, and only a small percentage of the gases unite to form ammonia; this small amount is absorbed in water or by liquefaction, and the remaining mixture of gases again passed over the iron catalyst (Fig. 127). The **Claude process** operates at 1000 atmospheres pressure, and the conversion is about 40 per cent. The gases are passed through a series of reaction chambers, the ammonia formed in each being removed as liquid ammonia by cooling the gas before its passage to the next member of the series.

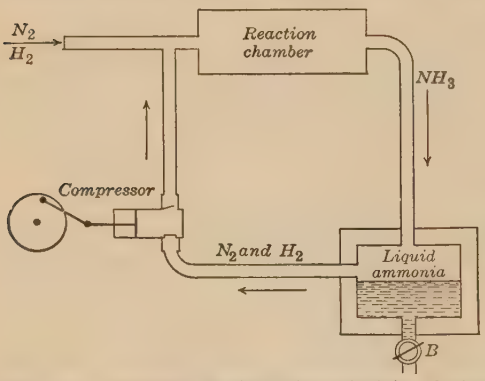

Fig. 127. Diagram to show the principle of the direct synthesis of ammonia.

The nitrogen and hydrogen are usually prepared from water gas. Water gas is essentially a mixture of nitrogen, hydrogen, and carbon monoxide made by the action of steam on hot carbon (coke). The carbon monoxide is removed by liquefaction, or the gas is mixed with steam and passed over a heated catalyst, which causes the carbon monoxide to react with the water as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The resulting gas contains nitrogen (originally present in the air), hydrogen, and carbon dioxide. The latter compound may be removed by treating the highly compressed gas with water.

236. Reversible reactions. The preparation of ammonia from the elements is another example of *a reversible reaction:*

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

We have already met a number of such reactions which will "work backwards" when the conditions are changed. The formation of carbonic acid (§ 121) and of ammonium hydroxide (§ 231) in water solution are two examples of reversible reactions, as is also the dissociation of ammonium chloride vapor (§ 232).

237. Kinetic equilibrium. We have stated that when a mixture of hydrogen and nitrogen is kept at 500° under pressure in contact with finely divided iron, a small amount and *only a small* amount of ammonia is produced. If we were to start with pure ammonia at the same temperature and pressure and in the same apparatus, we should find that almost all of it would be decomposed into nitrogen and hydrogen, but a *small amount of ammonia would remain unchanged.* Thus the final state of affairs in our closed apparatus would be the same whether we started with nitrogen and hydrogen *or* pure ammonia. Why is this so?

Suppose we could analyze the mixture in our closed reaction box continuously from the moment of mixing. We should find that when we started with nitrogen and hydrogen, the amount of ammonia increased rapidly at first; then the increase was slower, and finally the reaction apparently stopped when only a few per cent of ammonia was formed. No matter how long we waited we should get no more. It is evident that *either* the reaction has really stopped or *else* a balanced state of affairs is at hand. There seems to be no reason for the first possible explanation. Why should the reaction go to a certain extent and then the molecules cease interacting? It is very hard to

imagine such a condition or why the ammonia molecules should stop decomposing at precisely the same point. But an entirely satisfactory explanation of this puzzling situation is at hand if we give up the idea of cessation of chemical action and imagine rather that both the formation and decomposition of ammonia are proceeding but that *the two reactions are going at the same rate.* This state of affairs is called a *kinetic equilibrium.* From the point of view of the reacting molecules it is not a state of rest. The composition of the mixture (called the equilibrium mixture) is constant because we only examine the sum total of molecules and not the individual molecules, which are continually combining to form ammonia and splitting up again.

A rough analogy of what is going on in a system which is in chemical equilibrium is given by considering a large dance hall in which the music is continuous; there is a large crowd and a small dancing space. Perhaps fifty per cent of the people in the hall will be couples dancing; the others will be sitting or walking about. It might well happen that throughout the evening the proportion of dancers would be the same since as some became tired and stopped, others would take their places. This would then be a balanced condition, an equilibrium between individuals and dancing couples; yet any particular individual might stop and change partners a dozen times an hour.

238. Effect of catalysts. Nitrogen and hydrogen will stand at 500° without forming ammonia, and ammonia may be kept at the same temperature without decomposing. Both systems are **metastable** (unbalanced), however. If we introduce the right catalyst, a small fraction of the elements soon combine; or if we start with ammonia, all but a small fraction of it decomposes. The catalyst accelerates the speed of both reactions which in its absence are so slow as to be imperceptible; in a short time a balanced state of affairs (equilibrium) is attained. *A catalyst decreases the time required for a reaction mixture to come to equilibrium, but will not change the composition of the equilibrium.*

239. The effect of temperature. The composition of an equilibrium mixture is usually different at different temperatures. In the case of ammonia, the lower the temperature the higher the yield; with other reactions the reverse may be true. In view of the effect of temperature on the ammonia equilibrium, one may well ask, why operate at such a high temperature as 500°. The answer is to be found by remembering that the equilibrium state is not reached instantaneously but that it takes *time*. Both the formation and decomposition of ammonia proceed at a measurable speed. These rates depend on the concentration of the substances, the temperature, and the presence or absence of catalysts. With a given catalyst, the higher the temperature the sooner will equilibrium be attained. If an ammonia manufacturer had to wait a year for the maximum amount of ammonia to be formed, he could not make the process a success, even if the amount were as high as 80 per cent of the total. He therefore accelerates the process by using the best catalyst and an elevated temperature. He aims to use as low a temperature as possible, however, and still get a rapidly working process. The ideal catalyst would allow him to operate rapidly at room temperature or even at the boiling point of liquid ammonia (NH_3). But, alas, no such catalyst is known! The best catalysts now available cause a rapid reaction only at about 500° or above. For the present the chemist must be satisfied with that.

240. Factors affecting the rate of a reaction. We have just had an important example of the general effect of increase of temperature on the speed of a chemical process. The effect is usually very large, which explains why we so often heat things in the laboratory to make reactions "go." Usually a rise of 10° C. about doubles the speed of a reaction.

For example, the directions on a Kodak Development Tank state that when the solution is 70° F., the time needed to develop a photographic film is 15 minutes; at 65° F., 20 minutes; at 60° F., 25 min-

utes; and at 55° F., 30 minutes. This means that raising the temperature of the developer 15 degrees Fahrenheit (or 8.3° centigrade) makes it work twice as fast.

Another way of increasing the rate of a chemical process is to increase the amount of one of the reacting substances in a certain volume. Thus we have seen (§ 23) that charcoal and other materials burn faster in pure oxygen than in air (which is oxygen diluted with nitrogen). In a steamship the coal is burned under forced draft in order to supply the oxygen faster; that is, to increase the amount available at any one time. The amount of a substance in a given volume is called **concentration,** and we may therefore say that *the* ***speed*** *of a chemical process depends on the concentration of the reacting substances.* Increase the concentration and we increase the rate.

241. Law of Mass Action. In practical chemical work we usually want our reactions to continue in one direction until we obtain as much of the product as possible. We are sometimes able to do this in the case of reversible reactions by increasing the concentration of the reacting substances or by decreasing the concentration of the products. A mathematical statement of the relation of the concentrations of the substances in an equilibrium mixture is called the Law of Mass Action. A detailed consideration of this important principle is beyond the scope of an elementary course, but one or two examples of its use may be mentioned.

If we boil an ammonium hydroxide solution (§ 228), the ammonia gas escapes and more ammonium hydroxide decomposes into water and ammonia. Eventually all the ammonium hydroxide will have been transformed into water and ammonia gas, which has boiled out of the solution. The same is true for carbonic acid solutions. Other examples of the Law of Mass Action, which is sometimes called the Law of Molecular Concentration, will be met with in the chapter dealing with ionic reactions.

SUMMARY OF CHAPTER XX

AMMONIA (NH_3) is a colorless gas with a pungent odor, about half as heavy as air and exceedingly soluble in water. It is easily liquefied at ordinary temperatures.

In *nature* ammonia is formed by the putrefaction of animal and vegetable matter. In the *laboratory* it is usually prepared by heating ammonia water or a mixture of ammonium chloride and calcium hydroxide. *Commercially* ammonia is prepared as a by-product in the distillation of coal, and synthetically by the *Haber* and *Claude processes*, in which nitrogen and hydrogen combine directly.

CHEMICAL BEHAVIOR: ammonia *reduces copper oxide* to copper, forming water and nitrogen; ammonia reacts with hot magnesium, producing magnesium nitride and hydrogen; ammonia combines with hydrogen chloride to form ammonium chloride.

AMMONIA IN WATER SOLUTION is basic and contains the NH_4 and OH radicals of ammonium hydroxide.

AMMONIUM SALTS are prepared by neutralizing *ammonium hydroxide* with acids.

AMMONIA IS USED for refrigeration purposes, as a cleansing agent (in water solution), and as a source of ammonium compounds, and for the manufacture of nitric acid.

THE FIXATION OF NITROGEN means the process of manufacturing nitrogen compounds out of the free nitrogen of the air.

REVERSIBLE REACTIONS come to a condition of equilibrium, in which the two opposite reactions proceed at the same rate and the percentage composition of the mixture remains constant.

A CATALYST decreases the time required for a reaction mixture to come to equilibrium.

A RISE IN TEMPERATURE increases the speed of a chemical process. Increasing the concentration of the reacting substances increases the rate of a reaction.

THE LAW OF MASS ACTION states that by increasing the concentration of one of the reacting substances or by decreasing the concentration of one of the products, a reaction may go more nearly to completion in a given direction.

Questions and Problems

1. What is the difference between ammonia and ammonium?

2. What would be the action of dry ammonia on dry litmus paper? Why?

3. What two gases are sometimes used in refrigeration plants? What property have they in common?

4. How would you prove that ammonium hydroxide is a base?

5. Ammonia is sometimes spoken of as a basic anhydride. Explain.

6. What is meant by a reversible reaction? Give four examples from this chapter.

7. How would you test a salt for the presence of the ammonium radical?

8. Write the equation for the neutralization of ammonium hydroxide by sulfuric acid.

9. Ammonia is passed over hot copper oxide so as to produce 500 cc. of nitrogen. How many cubic centimeters of ammonia are required?

10. Ammonia is passed over hot magnesium so as to produce 1 liter of hydrogen. How many liters of ammonia are needed?

11. If 10 grams of magnesium nitride are put into water, how many grams of ammonia are produced?

12. If *aqua ammonia* is 35% by weight ammonia and has a density of 0.882 g. per cc., how many grams of ammonia are there in 100 cc. of the solution?

13. How many grams of ammonium chloride are required to react with slaked lime in order to give the ammonia required in Problem 12?

14. Show why the Law of Mass Action is important to the industrial chemist.

15. Why are catalysts so commonly used in commercial chemical processes?

16. Why is the "*fixation of nitrogen*" such an important chemical problem?

Topic for Further Study

Refrigeration. If possible, visit a cold-storage warehouse or an artificial-ice plant. What is the principal expense entailed in this method of refrigeration? Investigate the household refrigerator. Measure the temperature in a household refrigerator with a thermometer. What is the temperature in a cold-storage plant? In an ice-cream freezer? On what principle do the iceless refrigerators operate? (Cressy's *Discoveries and Inventions, Chemistry in Industry*, vol. 2.)

Review Questions

1. Describe an experiment to determine whether (*a*) a solution is saturated, (*b*) a colorless sample of water contains a dissolved solid, (*c*) water contains dissolved air, (*d*) a salt is deliquescent, (*e*) an acid solution is dilute.

2. Complete and balance the following equations, using formulas throughout:

(*a*) sulfur dioxide and water and sodium hydroxide
(*b*) ammonia (gas) and hydrogen chloride
(*c*) manganese dioxide and hydrochloric acid
(*d*) ammonium chloride and caustic soda
(*e*) lead nitrate and hydrogen sulfide

3. State briefly how you would prove that the atmosphere contains (*a*) nitrogen, (*b*) carbon dioxide, (*c*) water vapor.

4. An experiment showed that, when 2.16 grams of silver were treated with chlorine, 2.87 grams of silver chloride were formed. Calculate from this result the atomic weight of silver. Assume the atomic weight of chlorine is 35.5.

5. A gaseous compound contains 85.71 per cent carbon, and 14.29 per cent hydrogen, and has a specific gravity (referred to hydrogen) of 35. What is its formula? (Atomic weights: C = 12, H = 1.)

CHAPTER XXI

NITRIC ACID AND THE FIXATION OF NITROGEN

Saltpeter — nitric acid, preparation and properties — oxidizing agent — aqua regia — action with metals — nitrates — test for NO_3 radical — uses.

Fixation of nitrogen — direct ammonia process, cyanamide process, and direct oxidation process — explosives — nitrogen cycle in nature — nitrogen compounds as fertilizers.

Oxides of nitrogen — nitric oxide — nitrogen dioxide — nitrous oxide.

242. The problem of fixation of nitrogen. Nitric acid and the nitrates are important in our modern life because they are necessary in the manufacture of **explosives** and of **fertilizers.** The principal source of nitric acid and the nitrates was formerly the deposits of sodium nitrate in Chile. This supply is not only rapidly becoming exhausted, but it may at any time be cut off from the rest of the world through some such contingency as war. The atmosphere, however, contains enormous quantities of nitrogen from which it should be possible to synthesize nitric acid and its derivatives. In fact, a number of successful methods have been developed for doing this very thing; they are called processes for the **fixation of nitrogen.** In the last chapter we described the ammonia process and shall consider in this chapter two others which have been used commercially.

243. Saltpeter. Saltpeter, or **niter,** is known to most people as one of the ingredients of gunpowder and as a preservative for meats. It was formerly obtained from certain dry countries in Asia where a decomposition product of animal matter reacted with potash to form potassium nitrate (KNO_3). Another

similar compound, called **Chile saltpeter,** is found in great deposits in Chile and Peru (Fig. 128). This raw saltpeter,

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Fig. 128. Saltpeter fields in Chile.

"caliche," contains from 17 to 50 per cent of sodium nitrate ($NaNO_3$).

As long ago as the ninth century men knew how to make **nitric acid** (HNO_3) from saltpeter. They followed a method similar to our own and called the acid "aqua fortis" (strong water) because of its great chemical activity.

244. Preparation of nitric acid. Nitric acid is generally prepared by a process very like that used in the preparation of hydrochloric acid; namely, by the action of concentrated sulfuric acid on a nitrate. Sodium nitrate, as the most abundant of the nitrates, is mixed with concentrated sulfuric acid and heated in a retort. In the

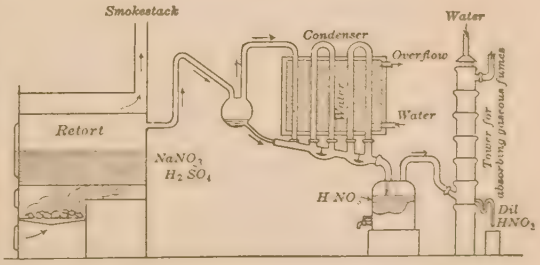

Fig. 129. Commercial preparation of nitric acid.

laboratory we take a tubulated glass retort for this purpose, but in the commercial manufacture of nitric acid an iron retort (Fig. 129) is used. The nitric acid is much more volatile than the sulfuric acid; hence it distills off and is condensed in a suitable apparatus. The substance left in the retort is sodium bisulfate:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \uparrow$$

In recent years considerable nitric acid has been manufactured by the oxidation of ammonia. This is done by heating a mixture of ammonia and air with some catalyst such as platinum:

$$NH_3 + 2\,O_2 \longrightarrow HNO_3 + H_2O$$

The process works at a relatively low temperature and therefore requires very little energy. The ammonia for this purpose is usually synthetic (§ 236), and the nitric acid produced is converted into nitrates (§ 249).

245. Properties. Pure nitric acid is a colorless liquid, boiling at 86° C. It fumes strongly when exposed to moist air. It is miscible with water in all proportions; the concentrated form which we buy contains about 68 per cent of the acid, the rest being water. Such a mixture has a density of 1.4 grams per cubic centimeter and boils at 120° C. It is highly corrosive, a few drops on the skin causing a bad burn. The dilute acid will turn the clothing and skin yellow.

Nitric acid can very easily be decomposed into water, nitrogen dioxide (NO_2), and oxygen. This decomposition takes place when the acid is merely exposed for a long time to sunlight. When the acid is heated strongly the decomposition is very rapid:

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2$$

Nitrogen dioxide is a red-brown gas which dissolves in water. When it dissolves in nitric acid, it gives the latter a yellow color. The so-called **fuming nitric acid** results if much of this oxide is dissolved.

We may show the decomposition of nitric acid by arranging a clay pipe so that the stem dips beneath the water, as in figure 130. When the stem is red-hot, a few drops of concentrated nitric acid are poured into the bowl. As the acid runs down the stem, it is decomposed into water, oxygen, and nitrogen dioxide. This latter gas dissolves in water,

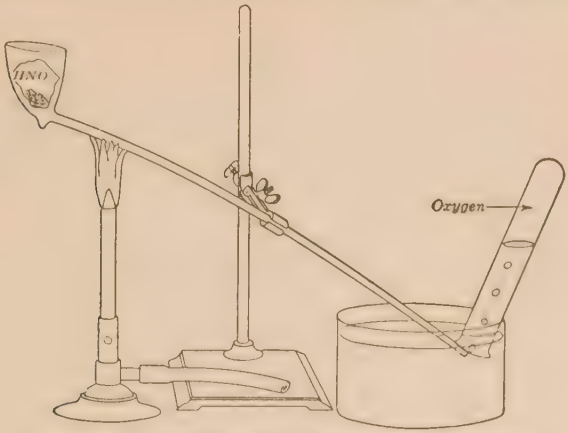

Fig. 130. Decomposition of nitric acid in a clay pipe.

and thus only oxygen is collected. The red-brown color which is characteristic of nitrogen dioxide can easily be seen when the bubbles first appear in the water.

246. Oxidizing action. Since nitric acid easily decomposes and gives off oxygen it is a good oxidizing agent. The equation which represents the decomposition of nitric acid when it acts as an oxidizing agent is as follows:

$$2\ HNO_3 \longrightarrow H_2O + 2\ NO + 3[O]$$

We indicate the fact that the oxygen is taken up by some other substance and is not itself set free by writing the symbol in brackets.

The oxidizing action of nitric acid can be shown by gently heating a small quantity of sawdust and putting two or three drops of concentrated nitric acid on the charred mass. This experiment is best carried

out in a crucible or porcelain dish (Fig. 131). The mass instantly takes fire, the charcoal burning at the expense of the oxygen from the nitric acid.

247. Aqua regia. Nitric acid oxidizes hydrochloric acid to water and free chlorine:

$$HNO_3 + 3\,HCl \longrightarrow 2\,H_2O + NO + 3[Cl]$$

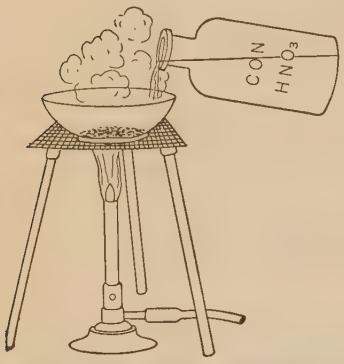

Fig. 131. Action of nitric acid on charred sawdust.

For this reason a mixture of one part of nitric and three parts of hydrochloric acid slowly evolves free chlorine, which at the moment of its liberation is very active. This mixture of acids, called **aqua regia,** will dissolve gold and platinum. We speak of an element at the moment of its liberation from a compound as being in the **nascent state;** most elements in this state are more active than in the free state. The nascent state we shall indicate by writing a bracket around the symbol. Since we do not know the molecular condition of a nascent element, we write a monatomic formula for it.

248. Action with metals. Nitric acid behaves differently from most acids as regards its action with metals. Free hydrogen is practically never produced by the action of even dilute nitric acid on metals. The reason is that the hydrogen, which is probably at first produced, is immediately oxidized to water by the nitric acid, the acid in turn being reduced to oxides of nitrogen. The exact product of the reaction depends on the concentration of the acid and the particular metal employed. In some cases the oxides of nitrogen may be further reduced to ammonia by the nascent hydrogen.

The most typical reaction is that of moderately dilute nitric acid on copper. The products in this case are copper nitrate, water, and nitric oxide:

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

The balancing of this equation is difficult and it will be found best to memorize it.

249. The nitrates. Nitric acid is a monobasic acid and forms salts, called **nitrates,** when neutralized by a base. Thus:

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

Besides dissolving all metals except gold and platinum, it dissolves a number of metallic oxides, such as copper oxide, forming the corresponding nitrate and water:

$$CuO + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

Nitric acid acts on such salts as will give a volatile product with the acid:

$$CaCO_3 + 2\,HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2\uparrow$$

Nitrates cannot be prepared by precipitation because the *nitrates of all metals are soluble in water.* We therefore often use the nitrate of a metal when we wish to work with a water solution containing a salt of that metal.

When a nitrate is heated, it generally decomposes into the metallic oxide, nitrogen dioxide, and oxygen:

$$2\,Cu(NO_3)_2 \longrightarrow 2\,CuO + 4\,NO_2 + O_2$$

But in the case of sodium and potassium nitrates the products are oxygen and a **nitrite:**

$$2\,NaNO_3 \longrightarrow 2\,NaNO_2 + O_2$$

Test for nitrates. We may easily recognize a nitrate by adding concentrated sulfuric acid and then heating with copper. The nitric acid which is formed acts on the copper, and *brown vapors appear.*

Minute amounts of the NO_3 radical may be detected by adding a solution of ferrous sulfate ($FeSO_4$) to the solution which is to be tested. Then concentrated sulfuric acid is poured in so as to form a layer below the mixed solutions. The *appearance of a dark brown ring* (Fig. 132) *just above the heavier sulfuric acid indicates the presence of the NO_3 radical.* The composition of this dark-colored compound is not definitely known. The test, however, is very delicate, and it requires some skill in manipulation.

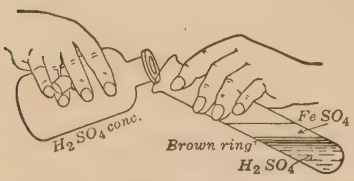

Fig. 132. Dark brown ring indicates a nitrate.

250. Uses. Nitric acid enters very extensively into the preparation of a number of organic compounds which are used as explosives and as intermediate substances in the preparation of dyes. The acid is also employed as a cleansing agent and for dissolving certain metals. The nitrates are very largely used as fertilizers. (See Industrial Chart, p. 181.)

Fixation of Nitrogen

251. The direct ammonia process. Because of its low energy cost, this is to-day the most important process. We have already discussed the direct synthesis of ammonia from the elements (§ 235). This ammonia may be converted into ammonium salts and used as fertilizers, or into urea ($CO(NH_2)_2$), which is a valuable special fertilizer. Synthetic ammonia can be oxidized to nitric acid (§ 244), and thus this process leads eventually to nitrates.

252. Cyanamide process. There is another ammonia process which is not so direct. Calcium carbide (CaC_2), which is used to generate acetylene, will combine with nitrogen when heated, forming carbon and a compound called calcium cyanamide ($CaCN_2$):

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

When this compound ($CaCN_2$) is treated with steam under pressure, it decomposes, forming calcium carbonate and ammonia:

$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3\uparrow$$

253. Direct oxidation. Nitrogen and oxygen will combine to a very slight extent at a very high temperature. The reaction is a reversible one and proceeds to the right as the temperature is increased:

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

At 2000° C. only about one per cent of the mixed gases combine; at 3000° C. about five per cent; while at ordinary temperatures the equilibrium mixture contains practically no oxide. If the mixture of nitrogen and oxygen is heated to 3000° C. and is then allowed to cool down slowly to room temperature, there will be no apparent change. The nitric oxide which was formed at the high temperature will keep reverting to its elements as the temperature is gradually lowered. If, however, the mixture is *quickly cooled*, the reaction does not have time to reverse itself completely, and a certain amount of nitric oxide will be left.

A number of commercial processes for directly oxidizing atmospheric nitrogen are based on this principle (Fig. 133). In all of these processes

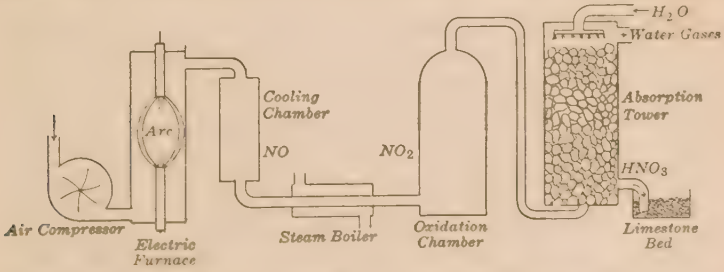

Fig. 133. Diagram of the Birkland-Eyde process of fixation of nitrogen.

air is blown through a flame produced between the electrodes of a powerful electric arc. In passing through this arc the air reaches a

high temperature and is then suddenly cooled as it leaves the flame. The gas from such a furnace contains about one per cent of nitric oxide. Since there is an excess of oxygen from the air in this mixture, the nitric oxide goes into nitrogen dioxide as the gas is cooled:

$$N_2 + O_2 \longrightarrow 2\,NO;\ \text{high temperature}$$
$$2\,NO + O_2 \longrightarrow 2\,NO_2;\ \text{lower temperature}$$

The gases are now led through towers down which water drips, and the nitrogen dioxide combines with the water, forming nitric acid and nitric oxide. The latter comes in contact with air and produces more nitrogen dioxide, which in turn reacts with the water. Thus, in the presence of air nitric oxide will completely dissolve in water, forming nitric acid:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$
$$2\,NO + O_2 \longrightarrow 2\,NO_2$$
$$4\,NO_2 + 2\,H_2O + O_2 \longrightarrow 4\,HNO_3$$

This nitric acid is neutralized with calcium carbonate, forming calcium nitrate, which is used chiefly as a fertilizer and as a source of nitric acid.

This method of making nitric acid (known as the Birkland-Eyde process) has worked successfully in Norway, where electric power is cheap on account of the abundant water power.

254. Explosives. An explosion is a very rapid chemical action in which a large volume of hot gases is produced from liquid or solid materials called **explosives.** The more rapid the action and the greater the quantity of gases produced, the more violent is the explosion. Old-fashioned **black powder** was a mixture of charcoal, sulfur, and potassium nitrate. On being ignited it burns suddenly with the evolution of a large volume of gases. If this action occurs in a confined space, such as a gun barrel, a strong expansive force is exerted.

Modern explosives are carbon compounds which contain nitrogen and oxygen. They are formed by the action of nitric acid on a number of different substances. They all have the property of decomposing quickly when they are ignited, or when another explosive is set off very near them. This latter process is called **detonation.** When they decompose *they pro-*

duce an enormous volume of gases at a high temperature, and these gases exert a terrific pressure, which does the work required of an explosive.

The explosive which forms the basis of the **smokeless powder** used in guns of all calibers is made by the action of nitric acid on cotton. Cotton is a compound of carbon, hydrogen, and oxygen, called cellulose, and the action of the nitric acid converts it into a compound called **nitrocellulose.** The nitrocellulose is turned into a jelly-like mass by certain solvents; this is pressed out into short rods or strips and dried. It burns in the barrel of a gun when ignited by the priming charge; the gases produced push out the projectile (Fig. 134). **Trinitrotoluene** (T.N.T.) and **picric acid** are the explosives used inside high-explosive shells, in mines, and in depth charges; they are produced by the action of nitric acid on toluene and carbolic acid respectively. These latter substances are prepared from coal tar. Trinitrotoluene (T.N.T.) and picric acid can be set off only by first exploding in them a more sensitive explosive (a detonator). They explode suddenly and with much violence, causing great damage.

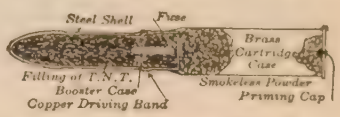

Fig. 134. Modern projectile used in the famous French 75 mm. gun.

Nitroglycerin is made by the action of nitric acid on glycerol ($C_3H_5(OH)_3$). It is a very sensitive explosive and is little used unmixed. When it is soaked up in sawdust or some other porous material, and mixed with sodium nitrate, **dynamite** is produced. Dynamite is too violent and sensitive an explosive to be used in guns or shells. It is used for blasting, for making large holes in the earth, and for wrecking purposes both in war and peace. It is extensively used in modern agriculture for blasting out stumps (Fig. 135), breaking up bowlders, blasting ditches, as well as in preparing the holes for the planting of trees.

All modern warfare is based on the prodigious use of explosives of all kinds, which in turn depend for their manufacture on

nitric acid. A belligerent country shut off from the supply of Chile saltpeter must have some method of producing nitric acid from the air, or else have large stocks of saltpeter stored up. In the recent great war Germany was able to continue fighting, only because her chemists had perfected the processes for the production of nitric acid from the air.

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Fig. 135. Getting a stump ready for blasting.

255. Nitrogen cycle in nature. Nitrogen compounds are an essential part of all living plants and animals. Those nitrogen compounds which occur naturally are called proteins; they are composed of carbon, nitrogen, oxygen, and hydrogen. The plant is able to build them up from the water, carbon dioxide, and the inorganic nitrates which it finds in the soil. The protein in animals is obtained entirely from the plants or other animals which they consume. The waste products of plant and animal life contain the nitrogen of the original protein combined in a number of different compounds, which are easily acted upon by

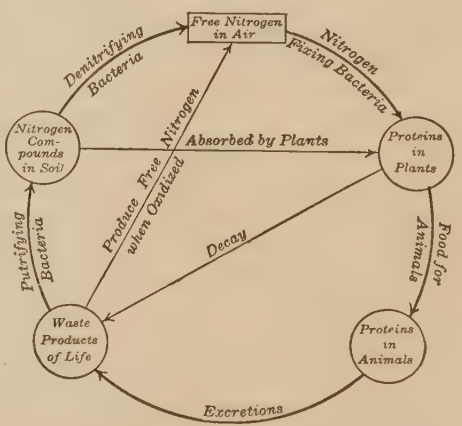


Fig. 136. Nitrogen cycle.

bacteria in the soil and turned into ammonium compounds. These ammonium compounds in turn are oxidized by other bacteria to nitrates, which can be taken up by plants (Fig. 136). Thus nitrogen makes a **cycle** through plant and animal life and the soil.

256. Nitrogen compounds as fertilizers. Unfortunately there are two factors at work upsetting this cycle. In the first place, there are certain bacteria which convert some of the nitrates of the soil into free nitrogen, which is thus lost. In the second place, in modern civilization the waste products of plant and animal life no longer find their way back to the soil; large quantities of them are forever wasted by being dumped into rivers and the sea. For these reasons nitrogen must be continually supplied to the soil in some form in which the plants can use it. If the waste products of life, such as manure, are available, they make an excellent fertilizer; but the supply is very limited. The artificial fertilizers which can be prepared by the chemist consist of ammonium compounds and the nitrates. Most of the nitric acid produced by the direct oxidation of nitrogen is converted into calcium nitrate, which is used directly as a **fertilizer.** In some localities calcium cyanamide can be used directly as a nitrogen fertilizer. The ammonia prepared from it, or prepared by the direct synthetic process, can be used as ammonium salts; or it may be oxidized to nitric acid and used as nitrates. *This problem of obtaining available nitrogen for plants from the atmosphere is one which will have great economic importance in the years to come.*

Fig. 137. Nodules contain nitrogen-fixing bacteria.

Some plants have themselves the power of converting the

nitrogen of the air into useful compounds. This is brought about by certain bacteria which are found in the tubercles on the roots of leguminous plants, such as peas and clover (Fig. 137). It is now possible to buy these bacteria and to inoculate beans and similar plants with them before planting. This insures the growth of the bacteria on the roots of the plant and consequently the direct production of a nitrogen fertilizer by the plant itself.

Oxides of Nitrogen

257. Oxides of nitrogen. Five oxides of nitrogen are known; only three of these are important. They are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Nitrogen trioxide (N_2O_3) and nitrogen pentoxide (N_2O_5) are unstable substances of no especial importance.

258. Nitric oxide (NO). Nitric oxide is most readily prepared by the action of dilute nitric acid upon copper. The equation for this reaction has already been discussed (§ 248). The apparatus is the same as that used to generate hydrogen. The gas is colorless and almost insoluble in water.

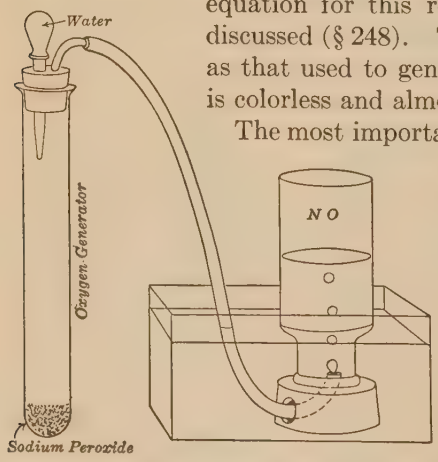


Fig. 138. Introducing oxygen into nitric oxide.

The most important property of nitric oxide is its ability to unite with oxygen, even at ordinary temperatures, to form a red-brown gas, nitrogen dioxide (NO_2):

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

259. Nitrogen dioxide (NO_2). This gas, which is formed when nitric oxide comes in contact with oxygen, has a very unpleasant odor and is poisonous when inhaled.

We may prepare nitric oxide as just described, fill a tube with it over water, and then introduce oxygen (Fig. 138), which can be conveniently generated by dropping water on sodium peroxide (Na_2O_2). As each bubble of oxygen enters the tube, it unites with the nitric oxide to form the red-brown nitrogen dioxide. But the color soon fades, and the water rises in the tube as the dioxide reacts with the water.

An interesting property of nitrogen dioxide is its reaction upon water by which nitric acid and nitric oxide are produced:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

When cooled this gas grows pale yellow, and its density becomes twice as great. This paler gas has the formula N_2O_4 and is called nitrogen tetroxide. At ordinary temperatures the gas is a mixture of the two; so we express the relation by a reversible equation:

At High Temperatures		At Low Temperatures
$2\,NO_2$	$\rightleftharpoons$	N_2O_4
(reddish-brown)		(almost colorless)

This is an excellent example of the fact that the condition of equilibrium of any chemical reaction depends on the temperature (§ 240). *For every temperature there is a certain ratio between the amounts of these two oxides.*

We have already seen that nitrogen dioxide plays the part of the carrier of oxygen in the manufacture of sulfuric acid by the chamber process (§ 187).

260. Nitrous oxide (N_2O). Nitrous oxide is the "gas" which the dentist uses as an anæsthetic. It was the first gas to be administered to a patient to render him temporarily unconscious of pain. Since it sometimes produces a kind of hysteria, it has been named "laughing gas."

It can be conveniently prepared by heating ammonium nitrate. This decomposes into water and nitrous oxide:

$$NH_4NO_3 \longrightarrow 2\,H_2O + N_2O\uparrow$$

The apparatus may be set up as shown in figure 139. The heat must be carefully regulated or an explosion may occur. The nitrate first melts and then begins to effervesce as it decomposes. One of the products is steam, which is condensed in the catch bottle; the other, nitrous oxide, is collected over warm water, in which it is but slightly soluble.

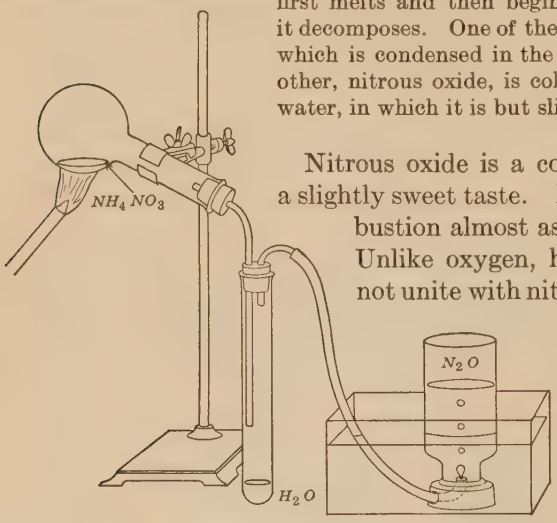


Fig. 139. Preparation of nitrous oxide.

Nitrous oxide is a colorless gas with a slightly sweet taste. It supports combustion almost as well as oxygen. Unlike oxygen, however, it does not unite with nitric oxide to form the brown dioxide. It will not support the combustion of sulfur unless it is burning vigorously. Nitrous oxide is easily liquefied and in this form is sold in steel cylinders. When it is used in minor operations, it is customary to mix it with air in order not to deprive the patient entirely of oxygen.

SUMMARY OF CHAPTER XXI

NITRIC ACID IS MADE by heating concentrated sulfuric acid and sodium nitrate and by the catalytic oxidation of ammonia. It is a colorless liquid which mixes with water. The commercial concentrated acid contains 32 per cent of water.

NITRIC ACID is easily decomposed, forming oxides of nitrogen and free oxygen. It is a powerful *oxidizing agent.* A mixture of nitric and hydrochloric acid is *aqua regia;* this furnishes nascent chlorine.

UNLIKE MOST ACIDS nitric acid very seldom produces free hydrogen with metals. *Oxides of nitrogen* are usually the products; in some cases ammonia may be formed.

NITRATES MAY BE PREPARED by the action of nitric acid on —

(1) metals, except gold and platinum;
(2) oxides and hydroxides;
(3) salts giving volatile products.

NITRIC ACID IS USED in the preparation of explosives, fertilizers, and dyes. Of the nitrates those of sodium and potassium are the most important. Sodium nitrite is made by heating sodium nitrate.

THE FIXATION OF NITROGEN means the process of manufacturing nitrogen compounds out of the free nitrogen of the air.

THE COMMERCIAL PROCESSES for the fixation of nitrogen include the following:

(1) the direct ammonia;
(2) the cyanamide process;
(3) the direct oxidation.

NITRIC ACID is used in the manufacture of all *explosives*. *Smokeless powder* is nitrocellulose and is made from cotton. The bursting charge in shells, mines, etc. is *trinitrotoluene* (T.N.T.) or *picric acid*. *Dynamite* is nitroglycerin absorbed in some porous material and mixed with sodium nitrate.

NITRATES are essential to plant growth. Nitrogen goes through a *cycle* in animal and plant life and the soil. This cycle is upset by several factors. For this reason nitrates must be applied to the land as *fertilizers*.

NITRIC OXIDE (NO) is prepared by the action of dilute nitric acid on copper. In contact with oxygen it produces *nitrogen dioxide* (NO_2), which is a red-brown gas, poisonous, and soluble in water. Nitrogen dioxide on cooling doubles its molecules and passes into *nitrogen tetroxide* (N_2O_4).

NITROUS OXIDE (N_2O) is made by heating ammonium nitrate. It supports combustion. It produces anæsthesia.

Questions and Problems

1. Why are the deposits of Chile saltpeter so valuable?

2. Why is sodium nitrate instead of potassium nitrate used in the commercial manufacture of nitric acid?

3. What is *aqua ammonia? aqua fortis? aqua regia? aqua pura?*

4. Explain how the chloride is formed when gold or platinum dissolve in aqua regia.

5. Name three metals which dissolve in nitric acid but do not dissolve in hydrochloric acid.

6. Name two acids which are strong oxidizing agents. Compare their properties (*a*) when in dilute solution and (*b*) when in concentrated solution.

7. State the law which is illustrated in the oxides of nitrogen. Explain.

8. How would you distinguish nitrous oxide from oxygen?

9. Write the chemical equations for the changes produced when the following nitrates are heated: (*a*) $Ca(NO_3)_2$, (*b*) $Cu(NO_3)_2$, (*c*) KNO_3, (*d*) NH_4NO_3, (*e*) HNO_3.

10. Concentrated nitric acid contains about 30 per cent of water, and concentrated sulfuric acid about 7 per cent of water. Explain why there is so much water in concentrated nitric acid.

11. How many grams of nitric acid could be made from 10 grams of sodium nitrate?

12. How many grams of nitric acid could be made from 10 grams of potassium nitrate? Compare this answer with that to Problem 11.

13. Calculate the density (grams per liter) of nitric oxide from the formula NO.

14. Compute the weight of copper which will be needed to generate with dilute nitric acid one liter of nitric oxide (standard conditions).

15. One liter of nitric oxide is converted into nitric dioxide by contact with the air. How many liters of air (approximately) will be required?

16. "Sulfate of ammonia" is a very concentrated commercial fertilizer. What per cent of nitrogen does it contain?

17. When black gunpowder is ignited, the reaction may be expressed in the following equation:

$$2\,KNO_3 + 3\,C + S \longrightarrow K_2S + 3\,CO_2 + N_2$$

(*a*) What are the approximate proportions (by weight) in which the three components of gunpowder are mixed? (*b*) What per cent of the products in the equation are gases?

Topics for Further Study

The fixation of nitrogen in the United States. What methods of fixing nitrogen are commercially possible to-day? What methods have been used on a large scale in this country? Why is the manufacture of nitrogen compounds from the air of national importance? (Slosson's *Creative Chemistry*, Duncan's *Chemistry of Commerce*, *U. S. Dept. of Commerce Bulletin No. 52* — Utilization of Atmospheric Nitrogen, Findlay's *Chemistry in the Service of Mankind*, and *Chemistry in Agriculture*.)

Explosives. Why are nitric and sulfuric acids considered the prime essentials for the manufacture of explosives? What other materials are needed for war-time explosives? for commercial explosives? What is the difference in action between smokeless powder, T.N.T., mercuric fulminate, and dynamite? How is each made? What explosives are used in mining and agriculture? (Martin's *Modern Chemistry*, Tilden's *Chemical Discovery and Invention*, and *Chemistry in Industry*, vol. 2.)

CHAPTER XXII

IONS AND ELECTRONS

Electrolytes and nonelectrolytes — abnormal behavior of electrolytes — ionization — electrolysis.

The electron — the vacuum tube — X rays — structure of salts — ions and atoms.

261. Solutions as electrical conductors. Solutions of different substances in water vary greatly in their power to conduct an electric current. Some solutions will not conduct the current at all; others conduct it very readily. Let us try to understand the reason for this difference.

We may study the conducting power of solutions, roughly, with apparatus somewhat like that shown in figure 140. The two platinum wires are connected with the electric circuit. The lamp which is on one of the wires serves as resistance to control the current, and also as an indicator of the current. When it glows brightly the solution is a good conductor.

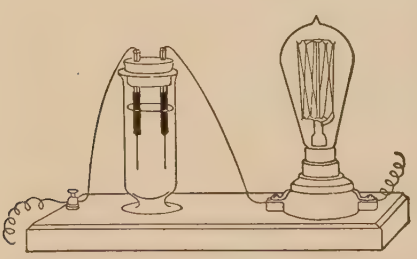


Fig. 140. Apparatus to show conductivity of solutions.

Let us use this apparatus to test distilled water and then solutions of sugar, common salt, hydrochloric acid, sodium hydroxide, acetic acid, ammonium hydroxide, and alcohol. We find that the lamp does not light when pure water or a solution of sugar or alcohol is used. But the solutions of salt, sulfuric acid, and sodium hydroxide cause the lamp to burn brightly, while the solutions of acetic acid and ammonium hydroxide give only a dull red glow to the filament.

It may have been noticed that in those solutions which conduct the electric current bubbles of gas rose from the electrodes; this indicated that a chemical change was going on. Solutions of acids, bases, and salts are called **electrolytes** because they conduct electricity; pure water and solutions like those of sugar and alcohol are called **nonelectrolytes.** *A chemical change always accompanies the passage of electricity through an electrolyte*, and in this respect these conductors differ from metallic conductors.

262. Other peculiarities of electrolytes. Solutions of acids, bases, and salts are peculiar in several other respects besides that of being electrolytes. In Chapter XVII we learned that one gram-molecule of a substance like sugar when dissolved in a liter of water lowered the freezing point from 0° C. to − 1.86° C., and raised the boiling point from 100° C. to 100.52° C. If one gram-molecule of sodium chloride or sulfuric acid is dissolved in a liter of water, the freezing point will be lowered and the boiling point raised; but *the effect will be about twice as great as with sugar.* All electrolytes behave in much the same way. So we say that acids, bases, and salts give *abnormal elevations* of the boiling point and *abnormal lowerings* of the freezing point.

Fig. 141. Svante August Arrhenius (1859–). Suggested the theory of ionization.

We have seen that the lowering of the freezing point and the raising of the boiling point depend directly on the number of

molecules present in a given weight of solvent. It would seem, therefore, as if an electrolyte contained a great many more particles of dissolved substance than did a nonelectrolyte. This can be accounted for if we assume that the *molecules of a substance like salt on dissolving in water break up into two or more parts* which are just as free as a molecule to move about in the solution.

Fig. 142. Michael Faraday (1791–1867). Made important discoveries in electricity and chemistry.

263. Ionization. On the basis of these facts a Swedish chemist, named Arrhenius (Fig. 141), suggested a theory which has been called the **theory of ions.** He supposed that when salt dissolved in water it was broken up into particles of sodium and of chlorine, and that each particle carried an electric charge, a positive charge in the case of sodium and a negative charge in the case of chlorine. This process is called **ionization;** to the charged particles Faraday (Fig. 142) had already given the name **ions,** meaning " wanderers." The following equation represents the change:

$$NaCl \longrightarrow Na^+ + Cl^-$$

NOTE. An ion is indicated by writing a + or − sign after and above the symbol.

These charged particles, or ions, must not be confused with atoms; they are atoms carrying an electric charge, but this electric charge completely modifies the nature of the particle. Particles of sodium could not be floating around in an aqueous solution, for sodium is a

very active metal which would immediately react with the water. The sodium ion is, however, quite different and does not react with the water.

We can now explain by the theory of ions the abnormal behavior of electrolytes in regard to the elevation of the boiling point and the lowering of the freezing point. Since the molecules split up into ions, we have, for example, in a solution of common salt twice as many particles as in an equimolecular solution of sugar, which is a nonelectrolyte.

264. Electrolysis. Let us now apply this theory to explain *two facts* about electrolytes; namely, that they *conduct* electricity, and are at the same time *decomposed* by the current. We shall suppose that we have some hydrochloric acid in a beaker with two electrodes dipping into the solution, as shown in figure 143. According to our theory the solution contains, besides the water (which is only very slightly ionized), hydrogen chloride (HCl) molecules, hydrogen ions (H^+), and chlorine ions (Cl^-), all flying around among the water molecules. When the electrodes are connected to some source of electricity, such as a generator (G) or a storage battery, one electrode becomes positively (+) charged and is called the **anode,** while the other electrode becomes negatively (−) charged and is called the **cathode.**

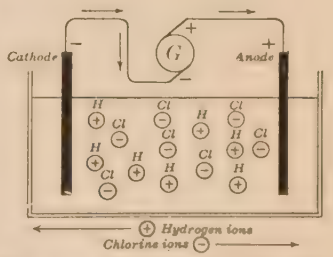


Fig. 143. Diagram illustrating the electrolysis of hydrochloric acid.

265. Theory of electrolysis. When the positive ions (H^+) come in contact with the negatively charged pole (the cathode), the charge on the ions is neutralized, and the result is ordinary hydrogen atoms. But we have already found that atoms of free hydrogen unite in pairs to form molecules (H_2), and so we notice bubbles of gas. At the same time the negative

ions are discharged at the anode, and chlorine is set free (at first largely dissolved in the hydrochloric acid). The discharge of the ions in the immediate vicinity of the two electrodes removes these ions from the solution. To take the place of the ions thus removed, other ions migrate toward their proper electrodes. Thus, when the circuit is closed, the ions move and actually carry electricity with them. Nonelectrolytes do not conduct electricity because they do not furnish the ions to carry it.

We thus find that the theory of ions gives us a very satisfactory account of the electrolysis of an aqueous solution, such as dilute hydrochloric acid. Sometimes the process is complicated by the fact that the atoms which are freed at the electrodes react with the water as fast as they are formed. This is the case with sodium hydroxide. The sodium atoms which are formed at the negative electrode immediately react, forming more sodium hydroxide and hydrogen. The hydroxyl ions, when the charge is removed, immediately break down into water and oxygen. Thus the gases which are produced at the two electrodes are hydrogen and oxygen, and sodium hydroxide is continually regenerated. The equations are:

at the *negative* electrode:	at the *positive* electrode:
$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2\uparrow$	$4\,OH \longrightarrow 2\,H_2O + O\uparrow$

266. The electron. When the ionic theory was first proposed, little was known about the nature of electricity, and very little was said about the nature of the charges on the ions. It was necessary to assume, of course, that there must always be an equal number of positive and negative ions, because a solution is electrically neutral; that is, it is neither positively nor negatively charged. Recent developments in physics have given us a clearer idea about the nature of electricity.

We now know that the **electron** is the *smallest quantity of negative electricity which can be transferred from one atom to another*. The electron has a mass about $\frac{1}{1845}$ that of the smallest atom (the hydrogen atom). Electrons may exist by themselves but are usually associated with matter. Physicists have shown us how it is possible to obtain streams of fast moving

electrons, and indeed how to measure their size and their charge.

In fact, we shall presently see that, according to modern theories, *matter is electrical in nature* and each atom has a positively charged nucleus surrounded by enough electrons to make the atom as a whole neutral. Accordingly, when an atom loses one or more electrons, it becomes positively charged (+ ion); and when an atom takes on one or more extra electrons, it becomes negatively charged (− ion).

267. The vacuum tube. If a glass tube containing air or some other gas is exhausted with a vacuum pump until there is only a very small amount of gas left, it exhibits unusual properties when connected with a high-voltage electric current (Fig. 144). The electricity passing through the tube gives it a peculiar bluish light. Such an apparatus is called a **vacuum tube.** Careful investigation has shown that from the cathode (the negative electrode) a stream of negatively charged particles is traveling in straight lines at high speed. These negative particles are the **electrons.** It has further been proved that from the positive electrode in the vacuum tube there is flowing a stream of positively charged particles of matter, which are the atoms of the original gas in the tube. They are positively charged because they have lost one or more electrons; they are gaseous ions.

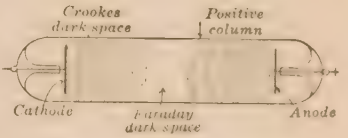


Fig. 144. Vacuum tube.

268. X rays. If we place a piece of metal in the path of the stream of electrons in the tube we have what is commonly called an **X-ray tube** (Fig. 145). When the electrons are stopped in their rapid flight by the piece of metal (anti-cathode), they produce a peculiar form of light energy, which passes through the glass and into the surrounding space. These are the so-called **X rays.** All light is supposed to be merely a vibration, or

wave motion, in the **ether,** that all-pervading material which has neither weight, volume, nor other physical or chemical properties. *X rays are vibrations in the ether which have a very short wave length* and are therefore much more penetrating than ordinary light. They are stopped by heavy metals but not by such materials as wood or paper.

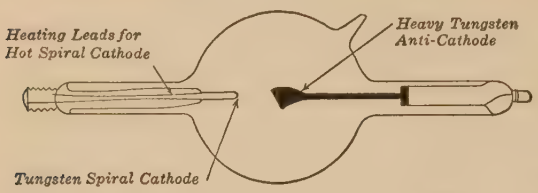


Fig. 145. X-ray tube as improved by Coolidge.

The penetrating power of X rays has led to their wide use in surgery and medicine. They affect a photographic plate exactly as does ordinary light. If, therefore, we place a hand or an arm between the X-ray tube and a photographic plate, we may make a radiograph with this penetrating light. Such radiographs are especially useful in dentistry in the examination of teeth.

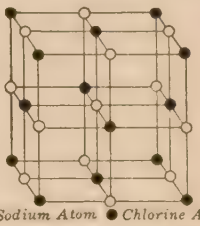
The rays may be rendered visible to the eye by the aid of a **fluorescent screen.** Certain minerals (zinc sulfide) give off light when X rays come in contact with them; they are said to **fluoresce.** By holding such a mineral screen in the path of the rays, we obtain a sort of shadow picture of the object through which they have passed.

Another peculiar characteristic of X rays is their power to discharge an **electroscope.** If an electroscope is charged with static electricity, the leaves will very slowly fall as the charge " leaks." If, however, the apparatus is brought near X rays, it will immediately be discharged. The reason for this is that the X rays break down some of the atoms of the surrounding air into gaseous ions, and these conduct the charge away from the electroscope.

269. The structure of salts. X rays have not only been of great practical value, but they have also enabled us to obtain a much clearer idea about the structure of solid salts and thus about

what happens when we dissolve a salt in water. The details of the method of investigating the structure of salts by means of X rays are complicated, and consideration of them belongs to the study of physics. What is necessary for the present is that we know the conclusions that have been drawn from this study.

It now seems fairly certain that a crystal of salt is made up of *ions* held together by electrostatic attraction. For example, solid sodium chloride contains positive sodium ions and negative chlorine ions which attract and hold each other in a solid form, just as all positively and negatively charged particles always attract each other (Fig. 146). When the salt dissolves in water, the ions are loosened from their mutual attraction and are free to move. The same is true if we melt a salt. Indeed, we find molten salts are excellent conductors of electricity. When a current of electricity is passed through a molten salt, the ions are discharged at the two electrodes just as in the case of an aqueous solution. Several important industrial processes depend on the electrolysis of fused salts.



○ *Sodium Atom* ● *Chlorine Atom*

Fig. 146. Atoms in a crystal of common salt.

270. Ions and atoms. Sodium chloride is made up of sodium ions and chlorine ions. But it must be remembered that these ions are very different from the neutral atoms of sodium in metallic sodium, or chlorine molecules in chlorine gas. The sodium ion is a positively charged sodium atom; the chlorine ion is a negatively charged chlorine atom. According to our present ideas the atoms of the elements themselves contain a minute nucleus of positive electricity and around this nucleus a sufficient number of electrons (negative electricity) to make the whole atom electrically neutral. *Ions are atoms which have gained or lost electrons.* Thus, the chlorine ion is an atom of chlorine *plus* one electron ($Cl + e$); the sodium ion is an atom

of sodium *minus* one electron (Na − e). In sodium chloride the sodium ion is positively charged because the atom has lost one unit of negative electricity; the chlorine ion is negatively charged because the atom has gained this negative electricity. The total number of the positive and negative ions is the same in a crystal of a salt. The solid is therefore electrically neutral.

271. Electron theory of electrolysis. The process of electrolysis is somewhat easier to understand now that we know more about the nature of electricity. A "current" of electricity is a stream of electrons flowing along a conductor. The two electrodes (Fig. 143) are thus paths by which electrons may enter or leave the solution. At the negative pole (cathode), the positive hydrogen ion may acquire an electron and thus become the neutral hydrogen atom. At the anode, the negative chlorine ion may deliver its extra electron and become the neutral chlorine atom. We may look upon the process of electrolysis as the removal of electrons from the negative ions and the addition of electrons to the positive ions of a compound. The ions must be free to move to the electrodes, and thus we use either the fused salt or a solution.

SUMMARY OF CHAPTER XXII

AQUEOUS SOLUTIONS which will conduct an electric current are called *electrolytes;* solutions which will not conduct the current are called *nonelectrolytes.* Solutions of acids, bases, and salts are electrolytes.

ALL ELECTROLYTES show an *abnormal* lowering of the freezing point and an *abnormal* raising of the boiling point.

THE IONIC THEORY assumes that in solutions of electrolytes the molecules are dissociated into charged particles called *ions.*

ELECTROLYSIS involves the discharge of the positive and negative ions at their respective electrodes with resulting chemical change.

THE ELECTRON is a tiny particle (or unit charge) of negative electricity. The mass of an electron is about $\frac{1}{1845}$ that of one hydrogen atom.

IN A VACUUM TUBE electrons (cathode rays) are shot off from the cathode surface. **X RAYS** are produced where these electrons strike a solid object or target.

BY MEANS OF X RAYS *salt crystals* have been found to be made up of *ions* held together by electrostatic attraction.

ATOMS OF ELEMENTS contain a minute *nucleus* of *positive electricity* and around this nucleus a sufficient number of *electrons* to make the whole atom neutral.

IONS are atoms which have gained or lost electrons.

Questions

1. How can you determine whether kerosene is an electrolyte?
2. What *four* series of *facts* indicate the truth of the theory of ions?
3. Define and illustrate the following terms: (*a*) *electrode*, (*b*) *electrolyte*, (*c*) *electrolysis*, (*d*) *ionization*, and (*e*) *electron*.
4. What are the properties of the hydrogen atom? of the hydrogen ion?
5. In what ways are X rays different from cathode rays (electrons)?
6. How is electricity conducted through electrolytes?
7. What classes of substances or solutions are conductors of electricity?
8. Why is the electron sometimes called the atom of electricity?
9. How are X rays different from ordinary light?
10. Where do ions occur besides in water solutions?

Topics for Further Study

Sir Humphry Davy and his brilliant pupil Michael Faraday. Which man did more for the advancement of chemistry, Davy or Faraday? (Moore's *History of Chemistry* and Thorpe's *Essays in Historical Chemistry*.)

Electrons and how we use them. What is the basis for the statement that all matter is composed of electrons and protons? Who discovered the electron? What generates the stream of electrons in a radio-vacuum tube? (Caldwell and Slosson's *Science Remaking the World*, and Russell's *A B C of Atoms*.)

CHAPTER XXIII

IONIC REACTIONS

Polar and non-polar compounds — acids and bases — weak acids and bases — neutralization — ionic reactions — ionic equilibrium — reactions which go to completion — valences in polar compounds.

272. Polar and non-polar compounds. Most salts conduct the electric current either when they are fused or dissolved. The commonest solvent for such compounds is water ; but certain salts dissolve in other liquids such as alcohol, and the resulting solutions are electrolytes. As we have seen in the preceding chapter, this behavior of salts finds an explanation in terms of the ionic theory. Compounds which readily conduct the electric current either in the liquid (molten) condition or in solution appear to be made up of ions. Such compounds are often called **polar compounds.** Most simple salts are in this class. Sugar, glycerol, fats, alcohol, and other substances which do not conduct by themselves or in solution are often called **non-polar.** It is probable that the molecules of such compounds do not contain charged particles but that the atoms are held together in some other way about which we are still ignorant. In the class with the non-polar compounds we must put the hydrogen molecule (H_2), the oxygen molecule (O_2), carbon dioxide (CO_2), and a great many other simple and important substances.

Between the two extremes of a polar compound (like salt) and a non-polar compound (like sugar) lie a number of substances about which it is more difficult to decide. For example, although a water solution of hydrogen chloride (hydrochloric acid) is an electrolyte, liquid hydrogen chloride is not. Indeed solutions of hydrogen chloride in many solvents other than

water are nonelectrolytes. Pure concentrated sulfuric acid is a nonelectrolyte, while a water solution of it is an excellent conductor of electricity. In water solutions these substances must be ionized; in the pure state they behave more like non-polar compounds. We cannot at present decide in what way the atoms in such compounds are held together. Perhaps the hydrogen chloride molecule is composed of an hydrogen ion and a chlorine ion; but more probably the nature of the union is more like that in the hydrogen or oxygen molecule, in which we have no reason to believe there are ions.

In this chapter we shall show how some of the common reactions of acids, bases, and salts can be easily understood as reactions of ions. The student must remember, however, that the ionic theory may be applied with certainty only to polar substances or solutions which conduct the electric current. The structure of non-polar compounds and their reactions seem to be a different matter.

273. Acids and bases. We can now more clearly understand the essential characteristics of acids and bases. When an acid like hydrochloric acid dissolves in water, it produces an hydrogen ion (H^+) and some other negative ion, in this case the chlorine ion. All acids give hydrogen ions, and we may thus define **acids** as *substances which dissolve in water and form hydrogen ions.*

All bases contain the hydroxyl group. On dissolving in water they dissociate into a positive ion, usually a metal, and the negative hydroxyl ion (OH^-). We can define **bases** as *substances which dissolve in water with the production of the hydroxyl ion.* All the characteristics of acids are really peculiarities of the hydrogen ion, and the characteristics of bases are due to the hydroxyl ion. In the case of dibasic acids, such as sulfuric acid, two hydrogen ions are produced; and in the case of bases, such as calcium hydroxide, two hydroxyl ions are produced:

$$H_2SO_4 \longrightarrow 2\,H^+ + SO_4^{--}$$

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2\,OH^-$$

274. Weak acids and bases. Water solutions of many acids are poorer conductors of electricity than a solution of hydrogen chloride or sodium chloride of the same molecular concentration. Such acids also attack zinc and other metals much less rapidly, and in many ways behave as if only a small proportion of the dissolved molecules had produced hydrogen ions. These acids are said to be **weak acids.** According to the ionic theory, their solutions contain many undissociated molecules, and only a small fraction of the total molecules are dissociated. We may write an equation representing this reversible process:

$$H_2S \rightleftharpoons H^+ + SH^-$$

In the same way some bases, such as ammonium hydroxide, are only slightly dissociated and are said to be weak bases. It must be remembered in comparing the strength of different acids and bases that we are comparing the *relative* degree of dissociation in *dilute* solutions. In order to compare the properties of the dilute solutions of two acids, we must take solutions of such concentration that there will be an equal number of molecules in a given volume of each solution. In such equimolecular solutions the strength of the acids will vary directly with the number of hydrogen ions.

Hydrochloric and nitric acids are strong acids. They are completely dissociated in dilute solutions. Sulfuric acid is also a strong acid. Acetic and sulfurous acids are weak acids; hydrogen sulfide and carbonic acids are exceedingly weak acids. Sodium, potassium, and calcium hydroxides are strong bases; ammonium hydroxide is a weak base chiefly because a large portion of the dissolved ammonia is present as NH_3 in solution (§ 231).

275. Neutralization. We have seen that when an acid and a base are brought together, water and a salt are formed. In terms of the ionic theory, this means that the hydrogen ion of the acid and the hydroxyl ion of the base unite to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

This reaction takes place because the molecules of water are very slightly dissociated. A molecule of water shows very little tendency to dissociate into a hydrogen ion and a hydroxyl ion. When we neutralize hydrochloric acid with sodium hydroxide, there are thus formed undissociated water molecules. The sodium ions and the chlorine ions are not affected; they still move around freely in the solution:

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$$

The solution, however, is electrically neutral since there are an equal number of positive and negative ions. We now have exactly the same condition at hand as if we had started with sodium chloride and had dissolved it in water. As we evaporate the solution it becomes more concentrated, and as soon as the solution becomes saturated, the ions begin to join together, and the solid crystalline sodium chloride separates.

276. Ionic reactions. Reactions in water solutions are characterized by the fact that nearly all of them occur almost instantly. The reason for this is that these reactions take place between ions. For example, an acid neutralizes a base so rapidly that we cannot measure the speed. In general, we can think of all reactions which take place in dilute solutions of acids, bases, and salts as being between ions. We can often write such reactions by forming equations in which the ions are shown; the neutralization reaction has already been written in this way.

The replacement of the hydrogen of an acid by a metal is really the transfer of the electron from a metallic atom to an hydrogen ion; the metallic atom is thereby turned into a metallic ion, and free hydrogen is liberated. Such a reaction can be represented thus:

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$

The negative ion of the acid need not be shown in such an equation because it is not involved in the reaction.

When we mix a solution of sodium chloride and potassium nitrate, nothing happens. The various ions merely move around freely in the solution. But when we make a mixture of sodium chloride and silver nitrate ($AgNO_3$), we at once get a white precipitate (AgCl). This is because the silver ions and chlorine ions combine to form the insoluble solid silver chloride (AgCl). In this way the reaction goes to completion: more and more silver ions and chloride ions unite, and more and more silver chloride is precipitated, until either the chloride ions or silver ions are exhausted:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

277. Ionic equilibria. Ionic reactions are practically instantaneous, and therefore the condition of equilibrium is reached as soon as we have mixed our solutions. All ionic reactions are probably reversible; but since many of them under ordinary conditions are more than 99.9 per cent complete, we usually write them with a single arrow. For example, not quite all the chloride ions and silver ions are precipitated when we mix equimolar amounts of sodium chloride and silver nitrate, because silver chloride is very slightly soluble in water and a correspondingly small amount of silver and chloride ions will be in the final solution. By adding a slight excess of silver ions or chloride ions we can decrease the amount of the dissolved silver chloride according to the law of mass action (§ 241). That is, the reaction will proceed farther to the right if we increase the concentration of either ion:

$$Ag^+ + Cl^- \longrightarrow \underset{\text{solid}}{AgCl\downarrow}$$

The product of the concentration of the silver ion and chloride ion in such a solution is constant; this product is sometimes called the solubility product. Thus we find in general that a precipitate is less soluble in a dilute solution of a salt with a common ion than in pure water.

From this point of view it is interesting to compare the mixing of sodium chloride with potassium nitrate on the one hand and with silver nitrate on the other. It is evident that the double decomposition reaction goes to practical completion in the one case because of the insolubility of silver chloride.

The neutralization of an acid by a base is also reversible, and we shall consider later (§ 286) cases where the reverse reaction is appreciable. With strong bases and acids the reaction goes to practical completion, however, because water is so very little ionized. The hydrogen ions and hydroxyl ions combine completely except for the very minute portion corresponding to the dissociation of water.

In general, we may say that on mixing solutions of polar compounds a reaction will take place only if the interaction of two oppositely charged ions produces an insoluble substance (solid or gas) or a slightly ionized substance.*

Fig. 147. Reaction goes to completion because a gas is evolved.

278. Reactions which go to completion. On the basis of what has just been said, we may divide all the double decomposition reactions which go to completion in water solution into *three classes:*

(1) If one of the products of the action is a **gas insoluble** in water, it will escape, and the action will therefore run to an end. Such a case is the action of dilute hydrochloric acid on sodium carbonate (Fig. 147):

$$2\,HCl + Na_2CO_3 \longrightarrow 2\,NaCl + H_2O + CO_2\uparrow$$

* This statement must be qualified if we are dealing with ions of variable valence, as oxidation or reduction reactions may occur (§ 442).

Fig. 148. Reaction goes to completion because a precipitate is formed.

When we mix dilute sodium chloride and dilute sulfuric acid, we do not get the same result, since hydrogen chloride is soluble in water. We merely have a mixture of the various ions. When we use concentrated acid and heat the mixture, a reaction takes place because hydrogen chloride is now expelled.

(2) Ionic reactions will go to completion if an **insoluble precipitate** is formed. This case has already been discussed in connection with the precipitation of silver chloride. Another example is the formation of barium sulfate (Fig. 148):

$$Ba^{++} + 2\ Cl^- + 2\ H^+ + SO_4^{--} \longrightarrow BaSO_4\downarrow + 2\ H^+ + 2\ Cl^-$$

(3) Ionic reactions will also run to completion if one of the possible products is **only slightly ionized.** The commonest example of this is the process of neutralization, which has already been considered (§ 275).

An interesting example of the combination of cases 2 and 3 is afforded by the reaction between sulfuric acid and barium hydroxide. If the conductivity of the solution is indicated by the ammeter reading (Fig. 149), it will be found that when neutralization is complete, the conductivity is reduced practically to zero.

279. Substances insoluble in water. In order to use the foregoing principles we shall need to know what substances are insoluble in water, or soluble only with difficulty. We have

already (§ 203) considered the case of gases. We shall now state some rules for the solubility of solids which it will be well to remember.

General Rules for Solubility

1. All *sodium*, *potassium*, and *ammonium* compounds are *soluble* in water.

2. All *nitrates*, *chlorates*, and *acetates* are *soluble* in water.

3. All *chlorides* are *soluble*, except those of silver, mercury (mercurous), and lead (lead slightly soluble).

4. All *sulfates* are *soluble*, except those of barium, lead, and calcium (calcium slightly soluble).

5. All *carbonates* are *insoluble*, except those of sodium, potassium, and ammonium.

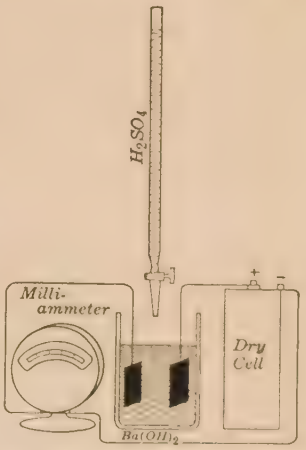


Fig. 149. Conductivity of solution depends on concentration of ions.

6. All *oxides* and *hydroxides* are *insoluble*, except those of ammonium, sodium, potassium, and barium (calcium hydroxide slightly soluble).

280. Valence in polar compounds. According to our present ideas concerning the structure of *polar compounds*, the crystalline solid is an orderly arrangement of positive and negative ions of such number that the whole is electrically neutral. **Metallic atoms** form *positive* ions by losing one or more electrons. **Non-metallic atoms** (like chlorine) or groups of non-metallic atoms (*e.g.* SO_4) become *negative* ions by acquiring electrons. *The number of electrons gained or lost by each atom* (or group of atoms) *in becoming an ion is the* ***valence of the ion.*** The valence of some common ions is given in the table on page 270.

VALENCE OF SOME COMMON IONS

POSITIVE IONS			NEGATIVE IONS		
Monovalent	Divalent	Trivalent	Monovalent	Divalent	Trivalent
H^+	Ca^{++}	Al^{+++}	OH^-	SO_4^{--}	PO_4^{---}
Na^+	Ba^{++}	Fe^{+++}	Cl^-	CO_3^{--}	
K^+	Mg^{++}		Br^-	SO_3^{--}	
Ag^+	Cu^{++}		I^-	S^{--}	
	Zn^{++}		NO_3^-		
	Fe^{++}		OCl^-		

Thus, when sodium and chlorine combine to form sodium chloride, the sodium atom loses one electron and the chlorine atom gains one (NaCl). When metallic calcium and chlorine react, however, each calcium atom gives up two electrons and becomes the doubly charged calcium ion; to take these two electrons requires two chlorine atoms. The compound is therefore calcium chloride, $CaCl_2$. When metallic zinc dissolves in sulfuric acid, the zinc ion is formed by the loss of two electrons; these are transferred to *two* hydrogen ions, which become hydrogen atoms. On evaporating the solution, each doubly charged positive zinc ion draws to it one doubly charged sulfate ion. The solid is zinc sulfate, $ZnSO_4$.

It is very useful in writing formulas of salts to remember the valence of the ions. If one then recalls that every compound must be electrically neutral, it is easy to see how many atoms must be combined together. For example, since the sulfate ion is doubly charged negatively, two single positive ions must be associated with it in sodium sulfate, for the algebraic sum of the total charges must be zero if an electrically neutral molecule is to result. Similarly, calcium sulfate must be $CaSO_4$ ($Ca^{++}\ SO_4^{--}$) and aluminum sulfate $Al_2(SO_4)_3$ ($2\ Al^{+++}\ 3\ SO_4^{--}$); any other combination would give an excess of positive or negative electricity.

SUMMARY OF CHAPTER XXIII

POLAR COMPOUNDS in the molten condition or in solution conduct electricity and are made up of ions.

NON-POLAR COMPOUNDS do not conduct electricity by themselves or in solution.

ACIDS are substances which dissolve in water and form *hydrogen ions.*

BASES are substances which dissolve in water and form *hydroxyl ions.*

IONIZATION of certain acids and bases is a reversible process, and is *complete only in dilute solutions.* Acids and bases which are only *slightly* ionized are said to be *weak.*

NEUTRALIZATION merely involves the combination of a hydrogen ion and a hydroxyl ion to form water.

IONIC REACTIONS will take place only if the interaction of two oppositely charged ions produces an *insoluble substance* (solid or gas) or a *slightly ionized substance.*

THE VALENCE of an ion is the number of electrons gained or lost by each atom (or group of atoms) in becoming an ion.

METALLIC ATOMS become *positive* (+) ions by losing one or more electrons.

NON-METALLIC atoms or groups of non-metallic atoms become *negative* (−) ions by acquiring electrons.

QUESTIONS

1. When dry sodium hydroxide is treated with dry hydrogen chloride, no chemical change takes place. Explain.

2. Define a salt in terms of the theory of ions.

3. What is the distinction between a *strong acid* and a *concentrated acid?* Between a *weak acid* and a *dilute acid?*

4. Write the ionic equation for the following reactions:

(*a*) Zinc and hydrochloric acid
(*b*) Potassium hydroxide and sulfuric acid
(*c*) Calcium hydroxide and hydrochloric acid

(*d*) Aluminum and hydrochloric acid
(*e*) Sodium and water

5. When cold concentrated sulfuric acid is added to zinc, there is no change. Explain.

6. When silver nitrate ($AgNO_3$) solution is added to potassium chlorate ($KClO_3$) solution, no precipitate is formed. When silver nitrate solution is added to potassium chloride (KCl) solution, a white precipitate is formed. Explain carefully.

7. Which of the following substances would you expect to be soluble in water: (*a*) *copper sulfate;* (*b*) *lead nitrate;* (*c*) *mercuric oxide;* (*d*) *barium hydroxide;* (*e*) *zinc nitrate;* (*f*) *sulfur dioxide;* (*g*) *tin oxide;* (*h*) *aluminum sulfate;* (*i*) *ammonium chloride;* (*j*) *calcium carbonate.* Give your reason in each case.

8. Write the formulas of the soluble substances named in question 7, and indicate the ions and the valences.

9. If one wishes to precipitate all the barium from a solution, why does he add an *excess* of sulfuric acid?

10. Explain clearly the distinction between *ionization* and *electrolysis.*

CHAPTER XXIV

SODIUM AND POTASSIUM COMPOUNDS

Sodium carbonate, manufacture by Solvay process - the two carbonates of soda, properties and uses — hydrolysis — other sodium compounds.

Potassium compounds — source and use as fertilizers — preparation of saltpeter. Metallic sodium and potassium — sodium peroxide — comparison with ammonium salts — flame tests — spectroscope.

281. Soda in the household and in industry. Probably everyone knows that there is in the kitchen — baking soda — and in the laundry — washing soda. What is the difference between these two substances? How are they made? Why are they used?

Soda is used by the carload in the manufacture of glass and soap. Formerly this soda was chiefly obtained from the ashes of plants growing in the salt marshes of Spain and was called **soda ash.** The French chemist LeBlanc to meet a national need discovered a way of making soda from common salt. Later a Belgian chemist Solvay invented a cheaper process. Therefore both sodium carbonate (washing soda) and sodium bicarbonate (baking soda) are fundamental raw materials used in the industries.

282. Solvay process. The older **LeBlanc process** has been largely replaced by the **Solvay ammonia process.** At Syracuse, N. Y., (Fig. 150) the process is carried out on an enormous scale. The principle of the process can be explained in three steps:

[1] Ammonia and carbon dioxide are dissolved in water, forming ammonium bicarbonate (NH_4HCO_3).

[2] This in turn reacts with sodium chloride, giving sodium bicarbonate ($NaHCO_3$) and ammonium chloride. The sodium bicarbonate, being only sparingly soluble in this solution, is precipitated.

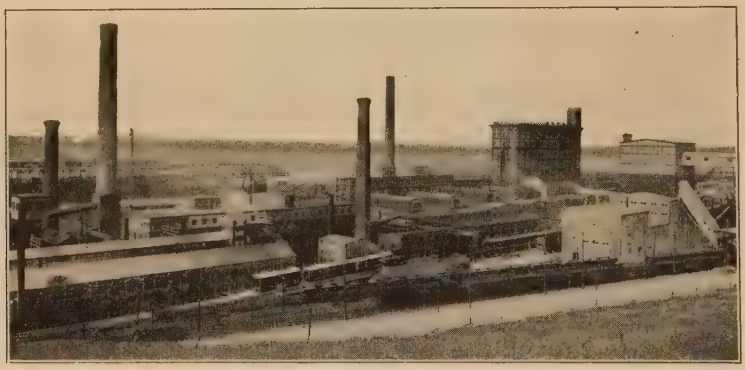


Fig. 150. General view of the Solvay works at Syracuse, N. Y.

[3] Finally, the bicarbonate on heating forms the carbonate. The reactions are as follows:

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3 \qquad [1]$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3\downarrow + NH_4Cl \qquad [2]$$

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad [3]$$

In the commercial process these reactions are carried out in the following manner: Brine from a salt well is saturated with ammonia gas and is then pumped into a carbonating tower. Carbon dioxide enters this tower at the bottom under pressure and is absorbed by the ammoniacal brine. The sodium bicarbonate comes down as a fine powder suspended in the liquid and is filtered off. The ammonium chloride is recovered from the solution by evaporation and is treated with lime in order to secure the ammonia for use again:

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3\uparrow + CaCl_2 + 2\,H_2O$$

In this way no ammonia is lost in the process. The carbon dioxide is obtained by heating limestone; the other product is calcium oxide, which gives with water calcium hydroxide:

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The calcium hydroxide is used for regenerating the ammonia, as just described. Thus we see (Fig. 151) that in this process the raw materials are calcium carbonate (limestone) and sodium chloride, two substances which can be obtained in large quantities very cheaply. The two products are sodium carbonate and calcium chloride. The latter has very little value and is for the most part thrown away.

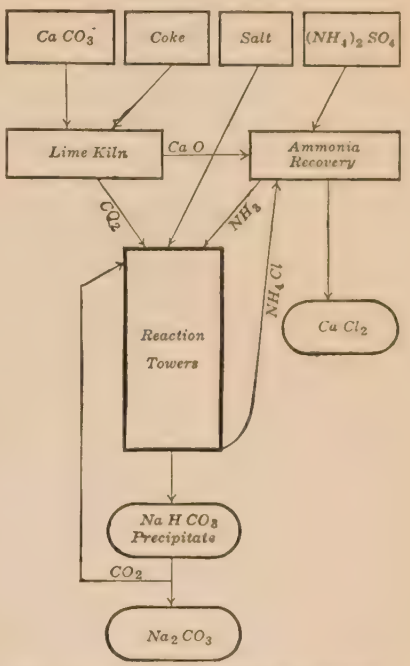


Fig. 151. Diagram of Solvay process.

283. The two carbonates of soda. Sodium carbonate forms large crystals containing ten molecules of water of crystallization ($Na_2CO_3 \cdot 10\ H_2O$). It is very soluble in cold water. Sodium bicarbonate ($NaHCO_3$) (sometimes called sodium hydrogen carbonate) is a fine, white, crystalline powder which is only sparingly soluble in water. When a solution of sodium carbonate in water is saturated with carbon dioxide, sodium bicarbonate is precipitated:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\ NaHCO_3$$

The reverse of this reaction takes place when sodium bicarbonate is heated, as in the last step of the Solvay process. Both substances react readily with acids, forming a salt and carbonic acid. Since carbon dioxide is but slightly soluble in water, the carbonic acid decomposes and the gas escapes; for these reasons the reaction runs practically to an end:

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2$$

Because the carbonates will react with acids, producing salts, they can be used instead of a hydroxide for neutralizing an acid. They are also used as a source of carbon dioxide. The fire extinguisher described in section 68 contained a solution of sodium bicarbonate.

284. Baking powders. Sodium bicarbonate is also an essential component of baking powders; hence it is often called baking soda. The other necessary ingredient of baking powders is some solid substance which is weakly acidic, such as cream of tartar, calcium acid phosphate, or alum. When the carbonate and the acid become wet, there is a reaction which results in a large volume of carbon dioxide gas, which leavens the dough. In some cases sour milk is used instead of the solid acid. Here the lactic acid reacts with the carbonate. Baking powders usually contain a small amount of starch or flour to keep them from deteriorating. In making so-called raised bread, yeast is used, which reacts with the sugar in the dough and by alcoholic fermentation produces carbon dioxide gas.

285. Sodium carbonate, or washing soda (Na_2CO_3). Sodium carbonate is often called washing soda because it acts as a mild alkali and yet is not so alkaline as to injure seriously the flesh or fabrics. Sodium carbonate is used in enormous quantities in the manufacture of caustic soda, soap, and glass. As we have seen (§ 281), it has long been called soda ash. (See Industrial Chart on page 181.)

Some of the sodium carbonate is put on the market as a dry powder, but another large part is sold as the so-called **soda crystals** ($Na_2CO_3 \cdot 10\,H_2O$). These crystals are transparent and contain ten molecules of water. They slowly crumble to a white powder consisting of the more or less dehydrated substance. This is an example of the process of **efflorescence.**

286. Hydrolysis. The reason why water solutions of sodium carbonate show an alkaline reaction when tested with litmus is easily seen if we consider the ionic reactions involved. Water is very slightly dissociated into H^+ and OH^-, and, although we have hitherto disregarded this dissociation, we now find it to be of importance. The carbonate ion (CO_3^{--}) combines with a certain number of hydrogen ions (H^+) from the water and thus produces carbonic acid (H_2CO_3). This is a very weak acid and is only very slightly dissociated; hence a number of undissociated carbonic acid molecules are formed in the solution, as shown in the following equations:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$Na_2CO_3 \rightleftharpoons 2\,Na^+ + CO_3^{--}$$

$$2\,H^+ + CO_3^{--} \rightleftharpoons H_2CO_3$$

For every ion of hydrogen which is thus removed by the formation of the undissociated molecules, there is left a hydroxyl ion in the solution. The result is that a solution of sodium carbonate contains a greater number of hydroxyl ions than hydrogen ions. Therefore it reacts alkaline; but only feebly so, for the concentration of the hydroxyl ions is necessarily small since they can be formed only to the extent that undissociated carbonic acid is produced. *The action of the ions of water on a dissolved salt is called* ***hydrolysis.*** It takes place whenever we are dealing with *the salt of a weak acid and a strong base, and results in an* ***alkaline*** *solution.* The weaker the acid, the more alkaline will the solution be.

It is interesting to note in this connection that the solution of sodium bicarbonate, often called acid sodium carbonate, reacts neutral with litmus.

We also have hydrolysis in the case of salts which are formed from a *strong acid and a weak base.* Here a certain concentration of undissociated base is produced, and an equivalent amount of hydrogen ions is set free, giving an **acid** reaction to the

solution; thus, ammonium nitrate, copper sulfate, and zinc chloride solutions all react acid with litmus.

Salts of strong acids and strong bases are not hydrolyzed, and the solutions give a ***neutral*** *reaction.* Such salts are sodium chloride, potassium nitrate, sodium sulfate.

287. Other important compounds of sodium. We have already described (§ 243) **sodium nitrate** as that valuable natural nitrate which is used as a source of nitric acid and as a fertilizer. A second important compound, called sodium thiosulfate ($Na_2S_2O_3$), is made by boiling a solution of sodium sulfite with sulfur. The hydrate is known as "**hypo**" ($Na_2S_2O_3 \cdot 5\,H_2O$) and enters extensively into the fixing process of photography and into the bleaching industry. Another salt is **sodium cyanide** (NaCN), a white solid with a strongly alkaline water solution. It is extensively used in extracting gold because it dissolves that metal in the presence of air. The compound itself is extremely poisonous, and in contact with acids evolves *the very poisonous hydrocyanic, or* ***prussic,*** *acid* (HCN), which is used to fumigate houses and orchards.

288. Potassium compounds. Potassium compounds are very similar to sodium compounds; we need consider them only very briefly. In general they are somewhat more soluble than sodium compounds and are therefore often preferred in the laboratory. Since they are more expensive, however, they are not used in the industries when the corresponding sodium salt will serve as well.

Potassium compounds are very widely distributed. They occur as the constituents of many igneous rocks; but these rocks are not suitable sources for obtaining the compounds commercially.

289. Potassium salts as fertilizers. In Chapter XXI we saw that nitrogen compounds are essential to the growth of plants. Potassium compounds are no less important in this regard. Most artificial fertilizers contain potassium salts, and the results of experiments like those shown in figure 152 prove that they are a valuable plant food. When plants are burned, the potassium compounds are converted into potassium carbonate,

which is found in the ashes. Thus wood ashes return needed potassium salts to the soil. By extracting wood ashes with water, potassium carbonate is produced. This was the old way of preparing potassium carbonate, which was called **potash.**

Since potassium compounds must be applied to the soil in order to produce the best crops, the question of the manner of

Courtesy of *Soil Fertility Lab., U. S. Dept. of Agr.*

Fig. 152. An experiment showing the effect of fertilizers on potatoes: 1. fertilizer lacking potassium salts; 2. no fertilizer; 3. fertilizer containing potassium salts.

obtaining them is vital. Potassium chloride is found in large deposits of mixed salts (carnallite) at Stassfurt, Germany, and this has hitherto been the principal source of supply, although other natural deposits have been found in certain places (*e.g.* in Utah) and have been used to a small extent. When the World War cut off the Stassfurt supply, considerable quantities of potassium compounds were produced in this country from our own mineral deposits, from the cement industry, in which they are a valuable by-product, and from the ash of one or two giant algæ of the California coast. Strangely enough, although most sea plants contain sodium compounds rather than potassium compounds, these algæ are an important exception.

290. Important potassium compounds. Potassium hydroxide, or caustic potash (KOH), is prepared exactly like sodium hydroxide and resembles this substance in its physical and chemical properties. In the laboratory it is used instead of sodium hydroxide for a few special purposes, but in general the reactions of the two are identical. Potassium carbonate and bicarbonate are very much like the corresponding sodium compounds, except that the bicarbonate is very soluble in water. Since the compounds of potassium are more expensive than those of sodium, they find only limited uses aside from that as fertilizers.

Potassium nitrate (KNO_3) is commonly called **saltpeter.** It is usually prepared from sodium nitrate by the following reaction:

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

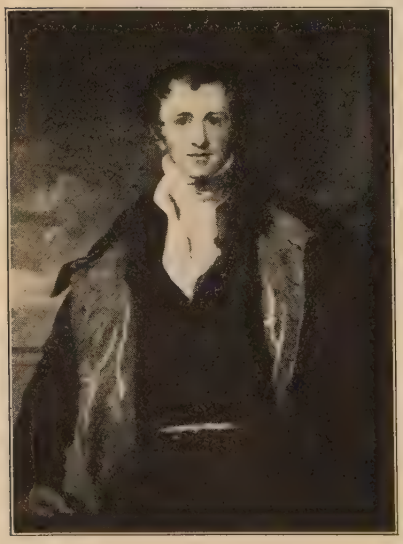


Fig. 153. Sir Humphry Davy (1778–1829). Brilliant English investigator who discovered sodium and potassium.

When hot saturated solutions of sodium nitrate and potassium chloride are brought together, the sodium chloride is precipitated and can be filtered off, leaving potassium nitrate in solution with only a little sodium chloride. The solution can then be cooled and the potassium nitrate crystallized out, as it is less soluble in cold than in hot water. This reaction depends upon the solubilities of the substances involved at various temperatures; the relationship is shown by the curves on page 187.

291. Metallic sodium and potassium. Metallic sodium is prepared by the electrolysis of fused sodium hydroxide. This operation was first carried out by Sir Humphry Davy (Fig. 153).

In the iron apparatus shown in figure 154 the molten sodium hydroxide conducts the current just as a solution of the substance does; oxygen is liberated at one electrode and the metallic sodium and hydrogen at the other. In the fused hydroxide, however, the metallic sodium finds no water with which to react and can be obtained in the free state. It is lighter than the fused hydroxide, floats to the top in a molten condition, and is ladled off from time to time. Metallic potassium is made in exactly the same way.

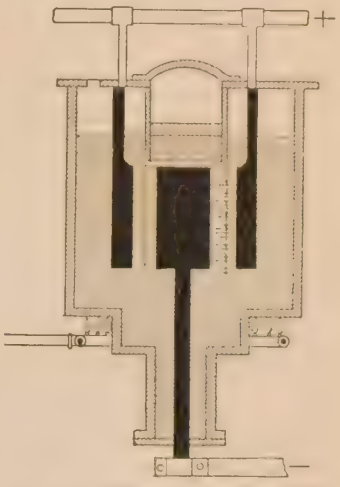


Fig. 154. Electrolytic cell for making metallic sodium.

Both metallic potassium and metallic sodium are very active substances and can be kept only if out of contact with the air. They are usually preserved under some such liquid as kerosene. When freshly cut both metals are silver white and very soft. They combine with most of the nonmetallic elements, such as oxygen and chlorine, with great energy. The reaction with water has already been discussed (§ 36). In the case of potassium the reaction is so violent that a piece of the metal takes fire when it is dropped on water.

292. Sodium peroxide. When metallic sodium is heated in air, it produces an oxide known as sodium peroxide (Na_2O_2). This oxide contains one atom more of oxygen than the normal oxide of sodium, and is a vigorous oxidizing agent; for that reason it finds many uses. Sodium peroxide reacts with water to form oxygen and thus furnishes a very convenient method of generating oxygen in the laboratory. Metallic sodium is prepared on an industrial scale for the preparation of this substance.

293. Comparison with ammonium compounds. In Chapter XX we studied the common compounds of ammonium (NH_4), such as the hydroxide, chloride, sulfate, and nitrate. These compounds are very similar to the corresponding compounds of sodium and potassium, in that the salts are white solids and are soluble in water, and in that the ammonium radical forms a monovalent positive ion.

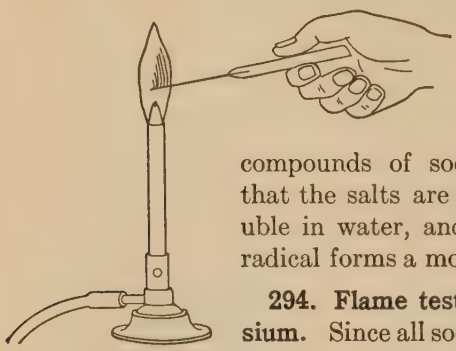


Fig. 155. Flame test for sodium.

294. Flame tests for sodium and potassium. Since all sodium and potassium compounds are soluble in water, we cannot test for them by any precipitation reaction. There is, however, one test for these elements which is extremely sensitive and which distinguishes them absolutely from every other substance. This is the color of the light which all sodium and potassium compounds, as well as the elements themselves, give out when they are heated to a high temperature.

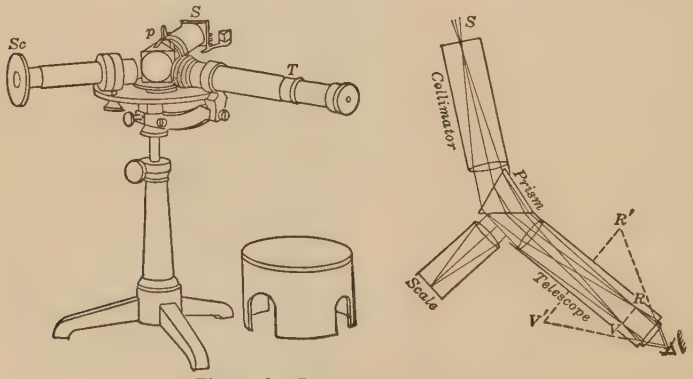


Fig. 156. Bunsen spectroscope.

We may hold a piece of clean platinum wire in the blue flame of a burner until all color disappears from the flame (Fig. 155). It may be

necessary to use a new burner to avoid impurities. We touch the wire to a sodium salt and bring it again to the edge of the flame. Then we repeat the experiment using a pure salt of potassium.

*The **yellow** color is a **test** for sodium.* This is so delicate a test that all the flames in a laboratory where sodium salts are being used show traces of yellow color.

*Potassium compounds color a similar flame **violet**.* This color is a **test** for potassium and its compounds but is easily obscured by the yellow color due to a trace of sodium. To obviate this difficulty the flame may be observed through a blue glass, which cuts out the yellow light and enables us to see the potassium flame if it is present.

Fig. 157. Robert Wilhelm Bunsen (1811–1899). Famous German chemist who invented the familiar laboratory burner, and who first used spectrum analysis.

295. Use of the spectroscope. A more exact method of testing for sodium and potassium is furnished by the spectroscope (Fig. 156). This instrument analyzes the light from the flame by means of a glass prism and shows a sharp, bright yellow line when sodium is present, even though the flame may be at the same time colored by more than this one substance. Other substances show characteristic lines when examined in this way (see Spectrum Chart). Some of them have a great many lines of varied colors; but none of the lines from different elements coincide exactly, and thus the presence of several elements in the same

substance can be detected. This method of analysis was used by Bunsen (Fig. 157) and Kirchhoff in discovering two new elements which resembled sodium and potassium, namely, cæsium and rubidium.

When the solar spectrum is studied carefully, we find that it is crossed by many vertical dark lines (see Spectrum Chart). These lines are called **Fraunhofer lines** and are caused by the presence in the outer layer of the sun's atmosphere of many gaseous elements which absorb certain characteristic portions of the light. The same effect may be observed in the laboratory if a beam of white light is passed through a sodium flame and then into a spectroscope; a dark line will be seen, which is in the same place in the spectrum as the usual *D* line of the sodium spectrum.

SUMMARY OF CHAPTER XXIV

ALL SODIUM, POTASSIUM, AND AMMONIUM SALTS are at least moderately soluble in water. Sodium, potassium, and ammonium ions are positive and monovalent.

THE CHLORIDES of sodium and potassium occur in nature and are used to prepare other compounds of these metals.

THE HYDROXIDES of these two metals are prepared by the electrolysis of the chloride solutions, or by the action of lime on the carbonate. They are strong bases.

THE CARBONATES occur in plant ashes. Sodium carbonate is manufactured by the *Solvay process.* This consists in the action of carbon dioxide on the ammoniacal solutions of the chlorides, which forms the bicarbonate. The carbonate is made by heating the bicarbonate.

THE CARBONATES ARE USED in washing powders and in making soap and glass. *Sodium bicarbonate* is one component of baking powders and is also used in chemical fire extinguishers.

SOLUTIONS OF THE CARBONATE are weakly alkaline, because of the excess of hydroxyl ions left by the formation of undissociated carbonic acid from the hydrogen ions of water. This action is called *hydrolysis.*

HYDROLYSIS is the action of the ions of water on dissolved salts. Salts formed by a weak acid and a *strong base* give *alkaline* reactions. Salts formed by a *strong acid* and a weak base give *acid* reactions.

POTASSIUM COMPOUNDS are essential for the growth of land plants and are therefore used as fertilizers. The chief source is the Stassfurt deposits in Germany.

METALLIC SODIUM AND POTASSIUM are made by the electrolysis of the fused hydroxides. They are very active substances. Metallic sodium is used to prepare *sodium peroxide*, an active oxidizing agent.

AMMONIUM compounds resemble potassium compounds in many respects.

SODIUM compounds color a Bunsen flame *yellow;* potassium compounds color the flame *violet.*

THE SPECTROSCOPE enables one to detect extremely small quantities of sodium and potassium by analyzing the light from the flame into characteristic colored lines.

Questions and Problems

1. What properties have ammonium salts in common with those of sodium and potassium?
2. Why is caustic soda cheaper than caustic potash?
3. Why are baking powders used in cooking?
4. What ingredient is common to all baking powders?
5. Explain why the water solution of sodium carbonate gives an alkaline reaction with litmus.
6. What are the most important uses of the two carbonates of sodium?
7. How could you distinguish in the laboratory between sodium carbonate and bicarbonate?
8. How would you test a compound for potassium in the presence of sodium?
9. Explain why a given weight of sodium hydroxide "goes farther" in neutralizing an acid than the same weight of potassium hydroxide.
10. Why is metallic sodium not prepared by the electrolysis of sodium chloride?

11. When a Seidlitz powder is dissolved in water there is much effervescence. Explain.

(Seidlitz powder contains tartaric acid in white paper and sodium bicarbonate and Rochelle salt in blue paper.)

12. What would happen in Question 11 if the patient took the contents of the papers *separately?* Don't try it!

13. Compare the solubility curves of sodium chloride and potassium nitrate. What practical use is made of this difference in solubility of these two salts?

14. What takes the place of baking powder in making "raised bread"?

15. Write the necessary equations to show the reactions involved in changing sodium chloride into sodium bicarbonate; sodium chloride into metallic sodium; sodium bicarbonate into sodium sulfate.

16. Write equations for the preparation of potassium hydroxide by three different methods.

17. If sodium bicarbonate costs $2.00 per 100 pounds, and sodium carbonate $1.40 per 100 pounds, which would be the cheaper for the preparation of carbon dioxide?

18. A certain fire extinguisher holds 2.5 pounds of sodium bicarbonate in solution. How many pounds of sulfuric acid (98% H_2SO_4) will be needed to set free all of its carbon dioxide?

19. How many pounds of sodium carbonate can be obtained from 100 pounds of sodium bicarbonate?

20. In the manufacture of 50 kilograms of sodium carbonate by the Solvay process, (*a*) how many kilograms of sal ammoniac would be formed and (*b*) how many cubic meters of carbon dioxide under standard conditions?

Topics for Further Study

Common salt. Why is salt said to be one of the foundation stones of all chemical industry? What is its direct connection with human life? What two substances which are made from it are found in every household? What is the cheapest source of salt? (Martin's *Modern Chemistry* and *Chemistry in Industry*, vol. 1.)

The chemistry of the stars. How has the spectroscope enabled astronomers to tell what chemical elements are present in the stars? What is the probable origin of the solar system? (Duncan's *Some Chemical Problems of To-day* and J. C. Philip's *Romance of Modern Chemistry*.)

CHAPTER XXV

THE HALOGEN FAMILY

Hypochlorous acid — properties — oxidizing action — chlorine water — hypochlorites — bleaching — disinfecting and antiseptic action. Bromine — occurrence, preparation, properties — hydrobromic acid — bromides. Iodine — hydriodic acid — iodides. Replacement of halogens. Fluorine — hydrofluoric acid. Comparison of the halogens.

296. The halogens. We have already studied the element chlorine and such compounds as hydrochloric acid and common salt. In this chapter we shall study about an acid containing chlorine and oxygen which is called hypochlorous acid (HOCl), and its salts, the hypochlorites. Then we shall consider briefly three other elements — fluorine, bromine, and iodine — which resemble chlorine in many respects and which together with chlorine are called the **halogens.** This family of elements is characterized by the fact that all the members are nonmetals with the valence of one. They form monovalent negative ions which are known as the chloride ion, fluoride ion, bromide ion, and iodide ion respectively. These ions are derived from the corresponding acids, which are water solutions of gaseous compounds containing one atom of hydrogen and one of the nonmetal.

297. Hypochlorous acid (HOCl). Chlorine water contains, besides the dissolved chlorine, some hydrochloric acid and hypochlorous acid. The reaction between water and chlorine which forms these two acids is reversible:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

Hypochlorous acid is known only in solution. The dilute solution shows the properties of a weak acid. *It is an extremely unstable substance* and tends to decompose, forming hydrochloric acid and oxygen according to the following equation:

$$2\,HOCl \longrightarrow 2\,HCl + O_2\uparrow$$

Because of this instability hypochlorous acid cannot exist in concentrated solutions.

298. Oxidizing action. Because hypochlorous acid so readily loses its oxygen, it is a powerful oxidizing agent even in a dilute solution. For example, it rapidly oxidizes sulfurous acid to sulfuric acid:

$$H_2SO_3 + HOCl \longrightarrow H_2SO_4 + HCl$$

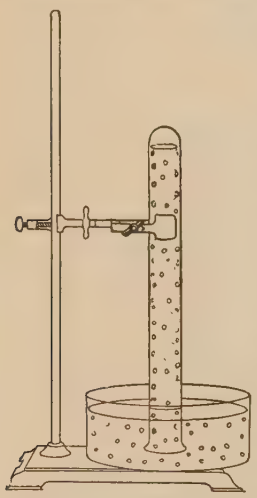


Fig. 158. Chlorine water decomposes in sunlight.

It will also oxidize many complicated organic compounds. It will oxidize hydrogen sulfide to water and free sulfur:

$$H_2S + HOCl \longrightarrow H_2O + HCl + S\downarrow$$

299. Chlorine water. Pure dilute hypochlorous acid is rather expensive to prepare. For almost any purpose chlorine water will serve equally well since the presence of hydrochloric acid in the solution does no harm. As fast as the hypochlorous acid is used up by a reducing agent, more of the dissolved chlorine reacts with the water and produces additional hypochlorous acid, until finally all the dissolved chlorine has been used up and converted into hydrochloric acid.

The slow decomposition of hypochlorous acid with the formation of free oxygen can be shown by filling a tube with chlorine water and allowing it to stand in the sunlight. A gas which can be shown to be oxygen collects in the top of the tube (Fig. 158):

$$2\,Cl_2 + 2\,H_2O \longrightarrow 4\,HCl + O_2$$

The oxidizing action of chlorine water can be demonstrated by treating a solution of sulfur dioxide with chlorine water. The sulfurous acid solution before such treatment will not give a precipitate with barium chloride in the presence of hydrochloric acid; but after it has been oxidized with the chlorine water a heavy precipitate is formed, showing the presence of sulfuric acid:

$$Cl_2 + H_2O + H_2SO_3 \longrightarrow H_2SO_4 + 2\,HCl$$

A solution of hydrogen sulfide in water forms a precipitate of sulfur on being treated with chlorine water, indicating that the oxidation has taken place:

$$Cl_2 + H_2O + H_2S \longrightarrow H_2O + 2\,HCl + S\downarrow$$

300. Hypochlorites. The salts of hypochlorous acid are called **hypochlorites.** They can be prepared by neutralizing hypochlorous acid, but they are more conveniently produced by other methods.

Sodium hypochlorite (NaOCl) is formed when chlorine is run into a *cold dilute* solution of sodium hydroxide:

$$Cl_2 + 2\,NaOH \longrightarrow NaOCl + NaCl + H_2O$$

What really happens in this case is that the sodium hydroxide neutralizes both the hypochlorous acid and the hydrochloric acid, which are in equilibrium with chlorine and water. Sodium hypochlorite can also be prepared by electrolyzing a solution of sodium chloride in a single narrow cell without a diaphragm. Chlorine is liberated at one pole, and sodium hydroxide is formed at the other. The two substances come in contact and form sodium hypochlorite. In both these methods for the preparation of sodium hypochlorites it will be noted that a dilute solution of the hypochlorite is formed which contains considerable sodium chloride; but the presence of this latter substance does not interfere with the usefulness of the hypochlorite.

The hypochlorites are unstable substances. On account of this instability they are always prepared and used in cold dilute solutions. On being warmed or on long standing they oxidize themselves into compounds containing more oxygen, called **chlorates.** Sodium hypochlorite solution, for example,

on heating gives sodium chloride and **sodium chlorate** ($NaClO_3$):

$$3\ NaOCl \longrightarrow 2\ NaCl + NaClO_3$$

Potassium chlorate we have already used; it is made by the action of chlorine on *warm* potassium hydroxide.

301. Bleaching powder (CaCl(OCl)). This substance is made by the action of chlorine on slaked lime. It is a white powder which is rather unstable and smells strongly of hypochlorous acid. Pure calcium hypochlorite has the formula $Ca(OCl)_2$. Bleaching powder acts very much like a **mixed salt** of calcium chloride and calcium hypochlorite, and has the formula $Ca\langle^{OCl}_{Cl}$ or CaCl(OCl):

$$Ca(OH)_2 + Cl_2 \longrightarrow Ca\langle^{OCl}_{Cl} + H_2O$$

Bleaching powder, or **"chloride of lime,"** serves as a commercial source of hypochlorous acid since lime is a cheap base. (See Industrial Chart on page 181.)

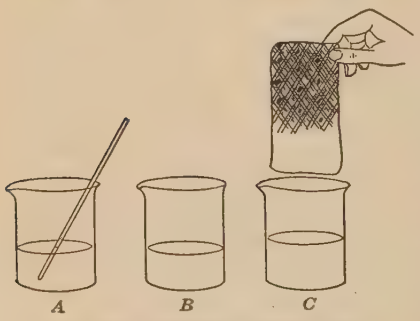


Fig. 159. Bleaching colored cloth.
A, dil. H_2SO_4; *B*, sol. of bleaching powder; *C*, H_2O.

302. Bleaching. Hypochlorous acid is a powerful bleaching agent; this is the most important use to which it and its salts are put. Most coloring materials are complicated organic substances which can be oxidized into colorless compounds. The oxidation is very readily accomplished by a dilute solution of hypochlorous acid, which sets free **nascent oxygen:**

$$HOCl \longrightarrow HCl + [O]$$

This action can easily be shown by dipping a piece of colored cloth in chlorine water or by suspending a piece of moistened cloth in an atmosphere of chlorine (Fig. 159). *Dry chlorine has no oxidizing action*, for it cannot form hypochlorous acid.

Bleaching is a very important process in a great number of industries. For example, most fabrics, such as cotton cloth, are colored slightly yellow by natural impurities and must be bleached before they can be put on the market. Figure 160 shows the general scheme

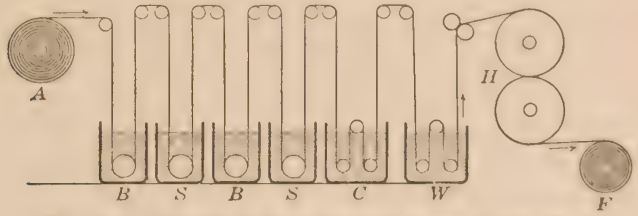


Fig. 160. Diagram of the commercial process of bleaching.

for bleaching cloth. The cloth passes through alternate vats of bleach (*B*) solution and very dilute sulfuric acid (*S*). In this way the hypochlorous acid is produced only within the fibers of the cloth, where it will be most effective. Then it goes through a solution of sodium sulfite (*C*) to destroy any remaining hypochlorous acid which might weaken it. Finally the cloth is washed in water (*W*) and ironed by passing over hot rolls (*H*).

Bleaching with hypochlorous acid is generally carried out in industrial works in one of the following ways: (1) chlorine water is prepared by running chlorine gas into cold water, and this solution is used directly; (2) sodium hypochlorite prepared by electrolysis or from chlorine gas and an alkali is used; (3) a suspension of bleaching powder in water is used. This latter method is the one commonly employed in the household. Fabrics must be thoroughly washed after being bleached in order to remove the chemicals, which would otherwise slowly rot the cloth.

Since hypochlorous acid is very weak, it is easily displaced from its salts by other acids. When a hypochlorite is treated with dilute acid, a solution of hypochlorous acid results, which can then act as a bleaching agent. In the commercial use of the hypochlorites this is accomplished, as described above, by

treating the material to be bleached first with the hypochlorite and then with dilute acid. When " bleaching powder " is used in the household, the acid required is slowly supplied by carbon dioxide in the air. The equations are:

$$CaCl(OCl) + CO_2 + H_2O \longrightarrow CaCO_3 + HOCl + HCl$$

$$HOCl \longrightarrow HCl + [O] \text{ used up in the bleaching.}$$

303. Disinfecting and antiseptic action. Diseases are caused and communicated by certain minute plants called **bacteria.** These microörganisms are generally present where there is much waste organic material. Hypochlorites readily oxidize such organic material and destroy the bacteria. For this reason " chloride of lime " has long been used in the household as a disinfectant. More recently a solution of sodium hypochlorite (prepared by the electrolysis of salt solution) has come into use for washing the floors and walls in hospitals and sick rooms.

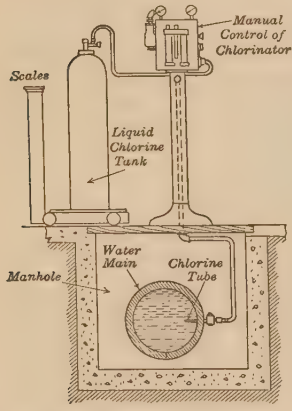


Fig. 161. Diagram illustrating the purification of water by chlorine.

Hypochlorous acid has recently been used as an **antiseptic agent** in surgery. Because of the sensitiveness of flesh to chemical reagents, it must be employed only in very dilute solutions and under certain special conditions. **Dakin's solution,** which has been found most valuable in dressing wounds, is essentially a solution of sodium hypochlorite, containing from 0.45 to 0.5 per cent of this substance. The solution must be made in such a way that it is practically neutral; if it were either alkaline or acid it would be too corrosive in an open wound. Furthermore, it is used most advantageously when the patient can be so arranged that a stream of the solution continually passes into the wound and washes it out.

The bacteria which are present in drinking water can readily be destroyed by hypochlorous acid. This is usually done by adding a small amount of a hypochlorite solution, or by running a small stream of chlorine gas from steel cylinders containing liquefied chlorine into the water supply (Fig. 161). About one part of hypochlorous acid in a million parts of water will completely purify all except the most polluted supplies. This method of purification has been adopted by many cities and towns.

Bromine

Bromine occurs as the bromides of sodium and magnesium in certain deposits of common salt. The bromides can be extracted and separated from the chlorides by crystallization, or the bromine can be freed directly and then converted into any desired bromine compounds.

304. Preparation. Bromine can be prepared in much the same way as chlorine; that is, either by electrolysis of a solution of sodium bromide, or by the oxidation of hydrobromic acid. If a mixture of sodium bromide and sodium chloride is electrolyzed, bromine is given off at the positive electrode before the chlorine. Advantage is taken of this fact in obtaining free bromine from the salt deposits just mentioned.

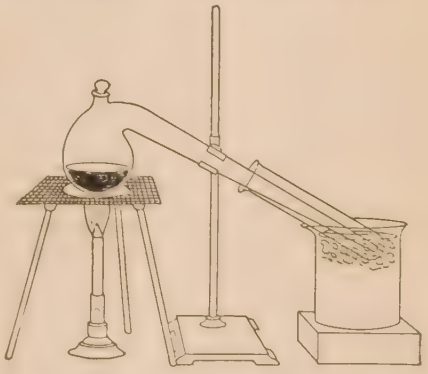


Fig. 162. Laboratory preparation of bromine.

In the laboratory we employ a mixture of manganese dioxide, sodium bromide, and sulfuric acid. The equation is similar to that for making chlorine:

$$2NaBr + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$$

The laboratory preparation of bromine is usually carried out in an apparatus called a retort (Fig. 162). The mixture of sodium bromide, sulfuric acid, and manganese dioxide is placed in the retort and gently heated. Bromine vapors fill the retort and condense in a cool receiver which is provided. Since bromine does not mix with water it is convenient to place some water in the receiver. A layer of bromine then collects under this water, and the fumes do not escape into the atmosphere.

305. Properties. Bromine is a dark, brownish red liquid, about three times as heavy as water; it is the only nonmetallic element which is a liquid under ordinary conditions. It has a strong, suffocating smell (the name bromine means a *stench*) and attacks the nose and throat, as chlorine does, and irritates the eyes. The liquid produces very painful burns on the skin, and great care should be taken in handling it It is somewhat soluble in water, and such a solution is commonly called **bromine water.** Like the aqueous solution of chlorine, it is an oxidizing agent.

Bromine is not quite so active as chlorine but combines readily with a number of elements with the evolution of much heat and light.

306. Hydrogen bromide. Hydrogen bromide is a gaseous substance similar in many ways to hydrogen chloride. It cannot, however, be satisfactorily prepared by the same reaction. When we heat sodium bromide and concentrated sulfuric acid, we produce hydrogen bromide; but this substance is so readily oxidized by the warm concentrated sulfuric acid that part of it becomes water and free bromine:

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + SO_2\uparrow + Br_2\uparrow$$

For this reason we use some other method when we wish to prepare hydrogen bromide. One way is to treat a mixture of red phosphorus and water with bromine. Red phosphorus and bromine combine to form the compound phosphorus tribromide (PBr_3). This compound immediately reacts with the water, forming pure hydrogen bromide and phosphorous acid (H_3PO_3), which is not volatile:

$$PBr_3 + 3\,H_2O \longrightarrow 3\,HBr\uparrow + H_3PO_3$$

Hydrogen bromide is a colorless gas, very soluble in water; its aqueous solution is known as **hydrobromic acid.** Hydrobromic acid is a strong acid. It is much more easily oxidized to water and the free element than is hydrochloric acid.

307. Bromides. The salts which are formed by neutralizing hydrobromic acid are called **bromides.** *All bromides are soluble except those of silver, lead, and mercury.* Silver bromide is a yellowish solid, used extensively in photography. The bromides of sodium and potassium are valuable as drugs.

Iodine

Iodine in the form of iodides occurs to a small extent in certain salt deposits. It is also found in the deposits of sodium nitrate in Chile. This is the principal source of the element, although it is also sometimes prepared from the ash obtained by burning certain seaweeds.

308. Preparation and properties. Iodine is prepared in exactly the same way as bromine and chlorine.

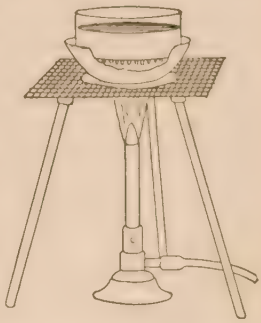


Fig. 163. Laboratory preparation of iodine.

The preparation of iodine can be conveniently carried out by warming a mixture of manganese dioxide, sulfuric acid, and sodium iodide in an evaporating dish on top of which is placed a dish containing cold water. The iodine vaporizes and condenses on the under side of the top dish, forming a mass of beautiful crystals (Fig. 163).

Iodine is a steel-gray solid which is very easily vaporized. The vapor has a beautiful violet color and on being cooled passes back directly into a solid. This process of passing from solid to vapor and back again without the formation of a liquid is called **sublimation.** Iodine is only slightly soluble in water, but is quite soluble in a solution of sodium or potassium iodides. It is also soluble in alcohol and is commonly sold in such a solution as **tincture of iodine.**

Iodine is less active than either of the other two halogens that we have considered; however, it will combine directly with many nonmetals at room temperature or when slightly warmed.

A very characteristic reaction of iodine is the formation of a blue color when a small amount is brought into contact with starch. *This reaction is employed as a* ***test*** *for either iodine or starch.*

309. Hydrogen iodide. Hydrogen iodide cannot be prepared by heating sodium iodide and sulfuric acid, for the same reason that this general method was impossible with hydrobromic acid. It is produced by the interaction of red phosphorus, iodine, and water. Hydrogen iodide readily dissolves in water and forms the solution called **hydriodic acid.** This acid is even more easily oxidized than hydrobromic acid and is therefore a good reducing agent. It is a strong acid, and on neutralization forms salts called **iodides.**

310. Iodides. *All iodides except those of silver, lead, and mercury are soluble compounds.* Silver iodide is a yellow, insoluble substance, and like silver bromide is used in photography. Certain iodides are necessary in the preparation of drugs; iodine itself is used in medicine.

311. The replacement of halogens. If we pass chlorine into a solution of a bromide or an iodide, we find that free bromine or iodine respectively is liberated and a chloride formed. This is a replacement reaction and is like the reaction in which metallic zinc liberated hydrogen from the hydrogen ion, except that we are now dealing with negative ions:

$$Cl_2 + 2\,Br^- \longrightarrow 2\,Cl^- + Br_2$$

$$Cl_2 + 2\,I^- \longrightarrow 2\,Cl^- + I_2$$

Bromine will liberate iodine from the iodide; but iodine will liberate neither bromine nor chlorine from their salts. We can therefore write these three elements as a series in which the higher member will liberate any element below it from its ion.

Replacement Series of Nonmetals
Chlorine
Bromine
Iodine

This table also indicates the **order of activity** of these nonmetals, that is, chlorine is most active and iodine is least.

Since chlorine is cheap and is easily obtained, it is sometimes used to liberate bromine or iodine from a solution of its salts and in this way to prepare the free elements on a large scale.

Fluorine

The fourth member of the halogen family differs somewhat from the others. This difference is more apparent than real and is due mainly to the fact that fluorine *is itself far more active than the other halogens and that its compounds are much more stable.* Fluorine occurs as a constituent of one or two important minerals, of which fluorite (CaF_2) and cryolite (Na_3AlF_6) may be mentioned. The former is used as the chief source of fluorine and its compounds. Fluorine compounds are somewhat poisonous and are used in large amounts in the manufacture of insect powders.

312. Preparation and properties. Fluorine is a slightly yellow gas, extremely poisonous and corrosive, and is very difficult to liquefy. It is the most active element known and at ordinary temperatures combines vigorously with most of the elements. Fluorine can be prepared only with difficulty. A French chemist, Moisson, in 1886 first isolated it by the electrolysis of a solution of potassium fluoride (KF) in liquid hydrogen fluoride (H_2F_2). The experiment had to be performed in platinum or copper apparatus as all other materials were attacked by the gas.

313. Hydrogen fluoride. Hydrogen fluoride can be prepared by the action of concentrated sulfuric acid on calcium fluoride:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2 \uparrow$$

It is a gas which is very soluble in water, forming an acid called **hydrofluoric acid.** Hydrogen fluoride is much more stable than hydrogen chloride and cannot be oxidized at all. It is easily condensed to a liquid, which boils at 19° C.

Hydrofluoric acid forms salts called fluorides. It is noteworthy because it will dissolve a great many substances, including sand (SiO_2) and glass. For this reason it is kept in wax bottles. Its action with sand results in the formation of the gas **silicon tetrafluoride** (SiF_4) and water:

$$SiO_2 + 2\ H_2F_2 \longrightarrow SiF_4\uparrow + 2\ H_2O$$

The action with glass takes place in much the same way since glass is a compound of silicon. This action of hydrofluoric acid on glass is taken advantage of in etching designs on that material. The glass is painted over with wax except where it is desired to have it etched, and hydrofluoric acid is applied (Fig. 164). After a time the acid is washed off and the wax removed; the glass is opaque where the acid has come in contact with it.

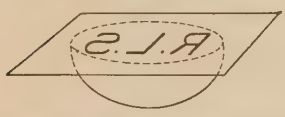


Fig. 164. Etching glass with hydrofluoric acid.

314. Comparison of the halogens. The following table summarizes the important physical and chemical properties of the halogen family, the elements being arranged in the order of their atomic weights. It should be remembered that the activity of these elements decreases progressively from fluorine to iodine, and that the stability of the hydrogen compounds decreases in the same order. This is also the order in which they replace each other. Fluorine is so active that it

Name	Atomic Weight	Boiling Point	State	Color
Fluorine (F) . .	19.0	− 187° C.	gas	pale yellow
Chlorine (Cl) . .	35.5	− 33.6°	gas	greenish yellow
Bromine (Br) . .	79.9	63°	liquid	red
Iodine (I) . . .	126.9	184.4°	solid	purplish black

replaces the oxygen of water. Because of this extreme activity it is to be regarded somewhat in the light of an odd member of the series; although its behavior seems more normal when we realize that it stands above chlorine in the family, and hence should be more active even than this active element.

SUMMARY OF CHAPTER XXV

CHLORINE WATER contains dissolved chlorine and hydrochloric and hypochlorous acids.

Hypochlorous acid is known only in solution; it is unstable, breaking down into hydrochloric acid and oxygen. It is a powerful oxidizing agent.

SODIUM HYPOCHLORITE is made by passing chlorine into cold sodium hydroxide or by electrolyzing sodium chloride. Sodium hypochlorite when warmed produces sodium chlorate.

BLEACHING POWDER, or *chloride of lime*, is made by the action of chlorine on slaked lime. It acts like a mixed salt ($CaCl(OCl)$).

THE HYPOCHLORITES AND HYPOCHLOROUS ACID are excellent *bleaching* agents and are used as such in the industries.

Hypochlorous acid is a *disinfecting* and *antiseptic agent* and is used in purifying drinking water. Chloride of lime is used as a disinfecting agent. *Dakin's solution* is one of the successful modern antiseptics which depend on hypochlorous acid for their action.

BROMINE is prepared from a bromide by heating with manganese dioxide and concentrated sulfuric acid. It is a dark red liquid which resembles chlorine in chemical properties but is less active.

HYDROBROMIC ACID is best prepared by adding water to phosphorus tribromide.

IODINE is prepared from an iodide by heating with manganese dioxide and concentrated sulfuric acid. It is a heavy, steel-gray solid which sublimes when heated.

HYDRIODIC ACID is a good reducing agent. It cannot be prepared from an iodide with sulfuric acid.

FLUORINE is the most active element known. It is prepared by electrolysis in a special apparatus. *Hydrofluoric acid* is made by heating calcium fluoride with sulfuric acid. It is used for etching glass.

CHLORINE will replace bromine and iodine from their salts; bromine will replace iodine; *fluorine* is so active that it replaces the oxygen from water.

Questions and Problems

1. What properties have all the halogens in common?

2. How could you distinguish bromine vapor from nitrogen dioxide?

3. How could you identify a chloride, a bromide, and an iodide?

4. Write the equations for the reaction of chlorine with hydrogen; with zinc; and with antimony.

5. How do you account for the smell of hydrogen sulfide which is produced when concentrated sulfuric acid is added to an iodide?

6. How would you test for free iodine?

7. What precautions must be taken in handling hydrofluoric acid?

8. How would you prove the presence of starch in beans?

9. How would you separate a mixture of iron and iodine?

10. What is the color of bromine molecules? of bromine ions?

11. Calculate the per cent of fluorine in fluorspar (CaF_2).

12. How many grams of silver nitrate would be needed to precipitate all the iodine in 20 cc. of a molar solution of potassium iodide?

13. How many grams would the precipitate in problem 12 weigh when carefully washed and dried?

14. How many kilograms of sodium chloride would be required to prepare 2 liters of chlorine gas at 20° C. and under a pressure of 5 atmospheres?

15. A compound contains 2.1% hydrogen, 12.8% carbon, and 85.1% bromine. At 140° C. and 76 cm., 1.00 grams of its vapor occupies 180 cc. Calculate its formula.

Topic for Further Study

Poison gas in the World War. What gas was first used in the war? When and where was the attack made? What other gases were subsequently used? In what form? (Slosson's *Creative Chemistry* and Auld's *Gas and Flame.*)

Review Questions

1. Compute the percentage of chlorine in hydrated barium chloride, $BaCl_2 \cdot 2\,H_2O$. (Atomic weights: Ba = 137, Cl = 35.5, O = 16, H = 1.)

2. Write equations for the following reactions, using formulas:
(*a*) ammonium nitrate (heated)
(*b*) copper and nitric acid (dilute)
(*c*) nitric oxide and oxygen
(*d*) ammonium sulfate and sodium hydroxide
(*e*) calcium bromide and chlorine

3. State briefly how you would prepare
(*a*) ammonium hydroxide from ammonium chloride
(*b*) nitric acid from sodium nitrate
(*c*) iodine from potassium iodide
(*d*) sodium sulfate from sodium chloride
(*e*) sodium carbonate from sodium chloride

4. Explain in terms of the ionic theory the changes which occur when an acid is neutralized by a base.

5. (*a*) What is the natural source of sodium compounds?
(*b*) How is metallic sodium prepared?
(*c*) How can the presence of sodium in a compound be shown?
(*d*) Give the formulas and uses of five compounds of sodium.

CHAPTER XXVI

THE NEW PERIODIC LAW AND THE STRUCTURE OF MATTER

Families of elements — properties and atomic weights — old and new periodic law — atomic numbers — periodic classification. Valence — metals and nonmetals — electrons and atoms — electrons and valence.

315. Families of elements. We have just seen that four elements — fluorine, chlorine, bromine, and iodine — form a family of closely related elements. Similarly, lithium, sodium, potassium, rubidium, and cæsium form the family known as the alkali metals. Other elements can be arranged in groups according to similarity in chemical properties. Such arrangements are very convenient in systematizing the chemical facts about elements, as it is possible to make certain general statements about all the members of the family. For example, *the alkali metals all react with water, their hydroxides are soluble and form strong bases, their ions have a valence of one and almost all the alkali salts of common acids are soluble in water.*

316. Properties of elements and their atomic weights. The existence of families of related elements points to the existence of some fundamental law in regard to the chemical properties of the elements. The Russian chemist Mendelejeff (Fig. 165) was the first who clearly showed how the elements might be arranged according to a definite system.

If we arrange all the elements in the order of their atomic weights (omitting hydrogen), we shall find that the eighth and sixteenth elements are fluorine and chlorine respectively, two

substances which resemble each other very closely. This relationship holds all through the first sixteen elements; if we write them as shown below, we note that similar elements fall in vertical pairs, as, for example, lithium and sodium.

He (4)	Li (7)	Gl (9)	B (11)	C (12)	N (14)	O (16)	F (19)
Ne (20)	Na (23)	Mg (24)	Al (27)	Si (28)	P (31)	S (32)	Cl (35.5)

We express the fact that similar elements reoccur in the series at certain definite intervals by saying that *the properties of the elements are a periodic function of their atomic weights.*

Fig. 165. Dmitri Ivanovitch Mendelejeff (1834–1907). A Russian chemist to whom we are largely indebted for the periodic system.

317. The old periodic law. This is the old periodic law, and it was remarkably successful in providing a satisfactory classification of the elements. The members of the various families, such as the alkali metals, found their natural place in such a system. There were, however, one or two apparent exceptions to the old periodic law. For example, if we place the elements strictly according to their atomic weights, potassium (39.1) comes after chlorine and is followed by argon (39.9). A glance at the arrangement given above shows that this order would place potassium under neon, and helium and argon under sodium and lithium. Of course, there is no doubt that chemically argon is like helium and potassium like sodium. To make a sensible arrangement, potassium in spite of its slightly higher atomic weight must be placed *after*

argon. Two other pairs of elements caused a similar difficulty. It was thought at one time that the atomic weights of these irregular elements must be in error, but repeated experimentation showed that this was not the case.

318. Value of periodic table. In spite of the exceptions, the periodic law as stated by Mendelejeff is a very great scientific generalization. Not only did it bring into one orderly scheme almost all known chemical phenomena, but it enabled Mendelejeff to make several bold predictions which were subsequently verified. In proposing the table, the Russian chemist was obliged to leave several blanks in order to put the known elements of similar properties in the same group. These blanks he believed represented undiscovered elements. On the basis of the position of these blanks he was able to predict with great accuracy not only the existence of these elements but their physical and chemical properties as well. His prediction was verified in three instances. The following table shows one of these; he prophesied the properties of what he called eka-aluminum, which when it was finally discovered was called **gallium.** There is hardly a scientific prediction in history that is more startling than this.

Properties of Gallium	Predicted	Found
Atomic weight	about 69	69.0
Melting point	low	30.1°
Specific gravity . . .	about 5.9	5.93
Action of air	none	slightly oxidized at red heat
Action on water . . .	decomposes at red heat	decomposes at high temperatures

319. The new periodic law. A young Englishman, Moseley, (Fig. 166) in 1912 laid the basis of a new periodic law which, unlike the old one, has no exceptions. Moseley was investiga-

Periodic Table showing Atomic Numbers and Valences

Period	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0		1 H (1) 1.008							
I	2 He (0) 4.00	3 Li (1) 6.940	4 Be (2) 9.02	5 B (3) 10.82	6 C (4) 12.000	7 N (5) 14.008	8 O (6) 16.000	9 F (7) 19.00	
II	10 Ne (0) 20.2	11 Na (1) 22.997	12 Mg (2) 24.32	13 Al (3) 26.97	14 Si (4) 28.06	15 P (5) 31.027	16 S (6) 32.064	17 Cl (7) 35.457	
III	18 A (0) 39.91	19 K (1) 39.096	20 Ca (2) 40.07	21 *Sc* 45.10	22 *Ti* 48.1	23 *V* 50.96	24 *Cr* 52.01	25 *Mn* 54.93	26 *Fe* 27 *Co* 28 *Ni* 55.84 58.94 58.69
		29 *Cu* 63.57	30 *Zn* 65.38	31 *Ga* 69.72	32 *Ge* 72.60	33 As (5) 74.96	34 Se (6) 79.2	35 Br (7) 79.916	
IV	36 Kr (0) 82.9	37 Rb (1) 85.44	38 Sr (2) 87.63	39 *Y* 88.9	40 *Zr* 91.	41 *Cb* 93.1	42 *Mo* 96.0	43 *Ma* ?	44 *Ru* 45 *Rh* 46 *Pd* 101.7 102.91 106.7
		47 *Ag* 107.880	48 *Cd* 112.41	49 *In* 114.8	50 *Sn* 118.70	51 Sb (5) 121.77	52 Te (6) 127.5	53 I (7) 126.932	
V	54 Xe (0) 130.2	55 Cs (1) 132.81	56 Ba (2) 137.37	57-71 Rare-Earths	72 *Hf* 180.8	73 *Ta* 181.5	74 *W* 184.0	75 *Re* ?	76 *Os* 77 *Ir* 78 *Pt* 190.8 193.1 195.23
		79 *Au* 197.2	80 *Hg* 200.61	81 *Tl** 204.39	82 *Pb** 207.20	83 Bi* 209.00	84 Po* 210.0	85——	
VI	86 Rn (0) 222.	87——	88 Ra* (2) 225.95	89 Ac* 227	90 Th* 232.15	91 Pa* 230?	92 U* 238.17		

The *atomic number* appears before the symbol of each element in red and the *atomic weight* below. The number of *valence electrons* is in parenthesis. The atomic weights of Po, Ac, and Pa are calculated values. At the places marked * are to be assigned a number of other elements, for the most part radioactive, which have the same chemical properties as the element in the table but somewhat different atomic weights.

ting X rays, those ether vibrations of very short wave length which are so much more penetrating than ordinary light (Chap. XXII). He discovered a method of spreading out X rays into a spectrum, which was, of course, invisible but could be photographed. His apparatus might be called an X-ray spectroscope. He used it for investigating the nature of the X rays emitted by various elements when they are bombarded by electrons in an X-ray tube, just as Bunsen many years before studied with a real spectroscope the visible light of the "sodium flame." The X-ray spectra of various metals, which Moseley used as anticathodes in his X-ray tube, had sharp lines of definite wave length, just as the visible light from many heated elementary vapors have definite lines, as shown by the periodic table. The number of lines in the X-ray spectra is less than is usually found in the case of visible spectra. Moseley now made the very important discovery that the wave length of the lines decreased regularly as he substituted one element for the next one of higher atomic weight. He could thus arrange the elements in such an order that the pairs of lines in the spectra of each appeared to have been progressively and regularly shifted in the directions of decreasing wave length as one passed from one element to another of higher atomic weight (Fig. 167).

Fig. 166. H. G. J. Moseley (1889-1915). An English physicist who determined the X-ray spectra of metals and laid the foundation for the use of atomic numbers.

This arrangement of the elements on the basis of their X-ray spectra is found to be exactly like the old series based on atomic weights, *except* that now the pairs of irregular elements are no longer reversed but fall into their proper places. *The chemical properties of the elements are a periodic function of their position in a series determined by their X-ray spectra.* Unlike the old periodic law involving atomic weights this statement is exact.

Fig. 167. X-ray spectra.

Since not all elements can be conveniently made into anticathodes, there are still some experimental gaps which obviously correspond to known elements; and there are in addition a few gaps corresponding to a very few elements which are as yet undiscovered. In recent years the X-ray spectrograph has been of great service in discovering new elements. Thus very recently hafnium, maesurium, rhenium, and illinium were first detected by the characteristic lines of their X-ray spectra (Fig. 168), which were found to have exactly the wave length *predicted.*

320. Atomic numbers. The number corresponding to the position of the element in this new series, if we take hydrogen as one, is called the *atomic number* of the element. A concise formulation of the new periodic law is, therefore, as follows: *The chemical properties of the elements are a periodic function of*

their atomic numbers. The atomic number is thus a more reliable criterion of the chemical properties of an element than the atomic weight. We shall consider some probable explanations of this in the closing sections of this chapter.

321. The periodic classification. The table facing page 305 shows the elements arranged in a periodic classification similar

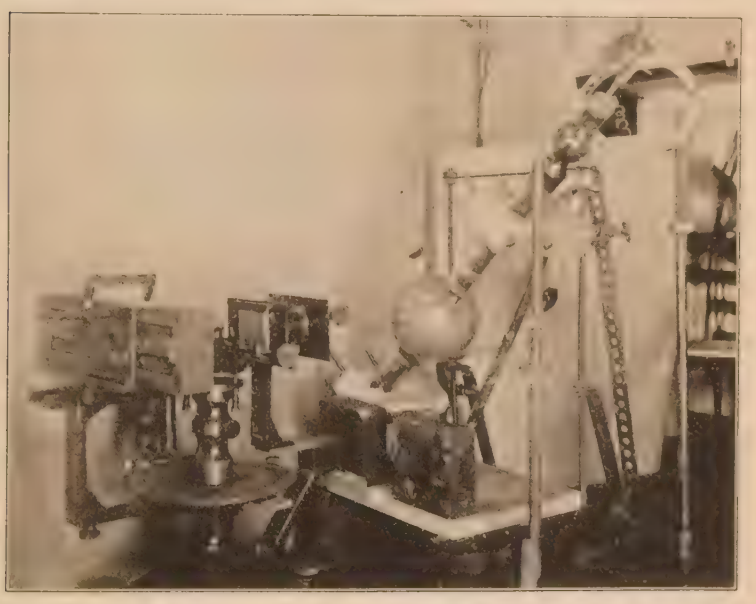


Fig. 168. X-ray spectrograph used by Professor Hopkins of the University of Illinois in discovering illinium.

to the one suggested by Mendelejeff but based on Moseley's law. The atomic number is printed in red before the element; the atomic weight under the element.

It will be seen that the elements fall into nine general vertical groups, the first of which is called the zero group and the last the eighth group. The third horizontal row starts with argon and ends with three elements, iron, cobalt, and nickel, which

are placed in the eighth group. The fourth row has no element in the zero group and is obviously somewhat different from the previous rows: it ends with the element bromine. The third and fourth rows of this table taken together are called a **long period;** the first and second rows are called **short periods.** Again, the fifth and sixth lines and the seventh and eighth make **long periods.** It will be noticed that *a long period has in the middle of it three elements which are put together in the eighth group;* this seems to take the place of the empty space in the zero group. The middle portions of the long periods have been inclosed by a heavy line, and the elements printed in italics. Such elements form a sub-group of each main group and are more nearly related to each other than to the other numbers. Thus, in the first group the alkali metals form one family, and copper, silver, and gold a different but related family.

322. Valence. The first important fact to be noted about the periodic table is that *all the elements which occur in a group have the same valence.* The elements in the zero group will not combine and may be considered as having a zero valency.

It will further be seen that as we proceed from left to right along any period the valence of the element increases regularly to the seventh. These regularities are very striking; when we remember that this classification of the elements is based solely on the position which they occupy in the series by virtue of their atomic numbers, it is even more extraordinary. The student may well familiarize himself with the position of the common elements in the table.

323. The nonmetals. In the first two periods (which are short periods) the members of groups VI and VII are active **nonmetals;** the elements of groups I and II are very active metals. In the long periods the three middle elements, which fall in group VIII, are all metals of a rather inactive sort; at the beginning of the period are active metals, and at the end of the period is an active nonmetal, such as bromine.

324. The metals. The very active alkali metals are together in group I; the subgroup of metals belonging to the middle of the long period (copper, silver, and gold) have the same valence in many compounds as the alkali metals, but are much less active, and their hydroxides are weak bases. It is interesting that the elements which have variable valency and which form colored ions occur in the middle of the long periods; as, for example, iron and copper.

In general, we may sum up by saying that *in the periodic system the most active metals are in group I: the most active nonmetals in group VII. Certain rather inactive metals lie in the middle of the long periods.*

The essential characteristic of a metal like sodium is its activity and the formation of a positive ion; this is sometimes called an extreme electropositive character. The essential characteristic of a nonmetal like fluorine is its activity and the formation of a negative ion; this is sometimes called an extreme electronegative character. With these definitions in mind we see that the most electropositive elements are in group I and the most electronegative elements in group VII. In between those extremes lie elements which represent the many gradations between these two opposite characteristics.

325. The electronic picture of an atom. What is the fundamental reason for Moseley's law? How can we explain the periodic variations in valency and other chemical properties? Indeed, how can we picture valence itself? These and similar questions have been much discussed by chemists and physicists since 1914, and we are now in a position to give a fairly satisfactory explanation of some of the many chemical phenomena which are included in the periodic classification. Much still remains in doubt, however, and the present explanation must be regarded as a working hypothesis and not a scientific generalization.

According to the general view now almost universally accepted by physicists, the atom is composed of a tiny nucleus surrounded

by electrons moving in orbits. The mass of the atom is in the nucleus. The negative charge of the moving electrons is exactly balanced by a positive charge on the nucleus. It is believed that the nucleus is the source of the X-ray spectra. Therefore the atomic number may be considered as a measure of the positive charge on the nucleus. This in turn is numerically equal to the number of electrons around the nucleus. Thus according to this hypothesis the position of the element in

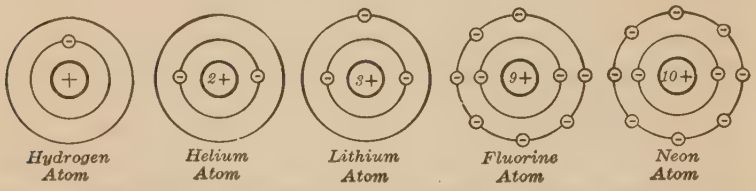


Fig. 169. Diagrams showing the structure of the atoms indicated according to the Bohr theory.

Moseley's series corresponds to the total number of electrons moving around the nucleus, and these electrons are responsible for the chemical properties of the element (Fig 169).

326. Electrons and valence. A satisfactory explanation of the valence of *polar compounds* of the first twenty elements has been developed from the electronic picture of the atom. The arrangement of the electrons in the rare gases is supposed to be such that in helium 2 electrons are moving together, in neon this group of 2 electrons is surrounded by a group of eight, and argon has still another ring of eight. Such arrangements of electrons are believed to be very stable, and the total lack of activity of the rare gases is thus explained.

All the others of the first twenty elements are supposed to have from one to seven extra electrons, which are largely responsible for the chemical properties (valence). The number of the extra or valence electrons is given in the table in parenthesis after the symbol. A stable arrangement, similar to that of a rare gas, can result by chemical combination between two elements

if one element gives its electrons to another to complete the group of eight (sometimes called an octet). This is probably what takes place in the formation of *polar* compounds. Thus, lithium gives its lone electron to fluorine, which has 7; the fluorine atom completes its group of eight and becomes the negative fluorine ion. The lithium, having lost its one extra electron, becomes the positively charged lithium ion (Fig. 170).

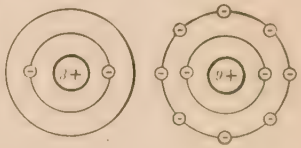


Fig. 170. Diagrams of the structure of ions (Bohr).

327. Electrons within the atom. *The valence of the metallic elements then is the number of electrons they may* **lose** *in becoming positive ions; the valence of nonmetals is the number of electrons they* **need** *in order to complete the group of eight.* Thus the valence of magnesium is 2 because it has two electrons which it may lose; but the valence of chlorine is 1 because it has seven electrons and needs only one to make the required eight.

The hydrogen atom is composed of a positive nucleus and a single electron. Like the atoms of the metallic elements, the hydrogen atom may lose an electron, forming a positive ion (H^+). Because of the peculiar fact that hydrogen behaves like a metal but is certainly not a metal, its position in the periodic table has been much discussed. The fact that it has only one electron is undoubtedly the reason for its peculiar behavior, and it is perhaps best omitted from the periodic classification or else placed in group 1.

The reason for the periodicity in chemical properties is nicely accounted for by the modern ideas concerning the atom. The transition from one element to the next of higher atomic number involves the increase of the positive charge on the nucleus by one and the number of valence electrons by one. Thus, from helium to fluorine we pass regularly from an element with no outer electrons to one with seven. The next transition to neon makes the total outer electrons eight, which is a stable grouping, and we again have a rare gas. The series from neon to chlorine

progresses in the same way; and the elements with the same number of outer electrons fall under each other in the same group, and therefore have the same valence. It should be noted particularly that among the first twenty elements the metals are those elements which have few valence electrons which they may lose. The nonmetals on the other hand are those elements with many valence electrons which acquire further electrons to complete the octet.

328. Unsolved valence problems. The problem of the nature of valence in nonpolar compounds is still unsolved. It is improbable that in carbon tetrachloride (CCl_4) the carbon has lost four electrons to the four chlorine atoms, since this compound shows none of the reactions of the chlorine ion. Similarly, in the hydrogen molecule (H_2) we are certainly not dealing with positive and negative hydrogen ions combined together. The most definitely polar compounds are those composed of extremely electropositive elements (groups I and II) and extremely electronegative elements (groups VI and VII). Difficulties are also encountered in interpreting the chemistry of the elements of atomic number higher than 20, in particular those elements which lie in the middle of the long periods. In spite of these complications and inadequacies, the electronic concept of valence is even to-day very useful in dealing with the polar compounds of the first twenty elements, and eventually we may hope it will give a clearer picture of all chemical phenomena.

SUMMARY OF CHAPTER XXVI

ALL THE ELEMENTS CAN BE ARRANGED in a table according to their *atomic weights*. The properties of the elements are a periodic function of their atomic weights with three exceptions.

A NEW PERIODIC SYSTEM arranges the elements on the basis of their X-ray spectra, and the chemical properties of the elements are a periodic function of their position in this series.

The number corresponding to the position of the element in this new series, if hydrogen is one, is called its *atomic number.*

THE NEW PERIODIC SYSTEM classifies the elements into nine groups. All the elements in a group have the same valence. The most active metallic elements are in group I, the most active nonmetallic elements in group VII.

ACCORDING TO THE ELECTRON THEORY an atom is composed of a tiny nucleus surrounded by electrons moving in orbits. The *negative* charge of the *moving electrons* is exactly balanced by the *positive* charge on the *nucleus.* The *atomic number* of an element is numerically equal to the number of moving electrons. The valence of the *metallic* elements is the number of electrons they may lose in becoming positive ions, and the valence of *nonmetals* is the number of electrons they need to complete a group of eight (an octet).

Questions

1. What does the phrase " periodic function " mean?
2. What natural processes might be called periodic?
3. Explain how Group 0 (the inert gases) fits into the periodic system.
4. What properties would you expect lithium to have?
5. What is the experimental basis for the *atomic number* of an element?
6. What part of an atom seems to determine the chemical properties of the element? Explain.
7. What part of an atom seems to determine its mass? Why?
8. Some writers call the atoms of metals *lenders* and the atoms of nonmetals *borrowers.* Explain.
9. Give three cases where elements are more naturally arranged in Moseley's table than in Mendelejeff's.
10. Describe three ways in which chemists have made use of the periodic system.

CHAPTER XXVII

THE PHOSPHORUS FAMILY

Family characteristics. Phosphorus, its preparation and properties — matches — phosphoric acid — phosphates as fertilizers. Arsenic and antimony. Bismuth. Useful alloys.

329. Family characteristics. The elements nitrogen, phosphorus, arsenic, antimony, and bismuth form a family which is often referred to as the phosphorus or nitrogen family. An inspection of the periodic table (page 305) shows that these elements fall in the fifth group, and each one is the third from the end of the period (short or long) in which it occurs. A regularity in chemical behavior is thus to be expected from what we have learned in the preceding chapter and, indeed, is found. The oxides of the members of this family are all acidic, just as are sulfur dioxide and sulfur trioxide. Indeed, nitric acid and its salts have already been discussed. It is interesting that the salts of phosphoric acid are essential to the growth of plants and, like the nitrates, are of prime importance in the manufacture of fertilizers. Compared to the alkali metal family or the halogen family, the phosphorus family is more individualistic. The members show marked differences one from another. These differences, however, are in reality only a gradual modification of properties which vary progressively with increasing atomic weight.

Phosphorus

330. History and occurrence. This element was discovered in the middle of the seventeenth century by an old philosopher (alchemist) named Brandt, who was searching for some substance

which would change everything into gold. But it was not until 1833, when matches began to be manufactured, that phosphorus became at all common or cheap.

The element is found in nature in the form of phosphates. Bones and teeth contain a large amount of calcium phosphate ($Ca_3(PO_4)_2$), which gives to them their necessary hardness and rigidity. The muscles, nerves, and brains of animals contain very complex organic compounds of phosphorus. These are formed in the body from the phosphorus compounds which are contained in almost all vegetable food. The plants in turn need soluble phosphates in the soil for their growth.

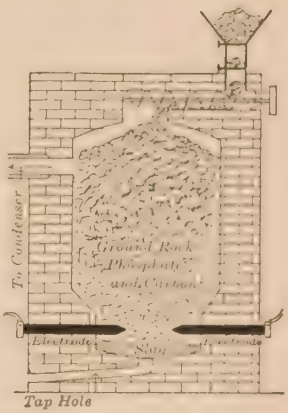


Fig. 171. Electric furnace used to prepare phosphorus.

331. Preparation. Phosphorus is obtained from the mineral calcium phosphate, which is mixed with coke and sand (SiO_2) and heated in a suitable electric furnace (Fig. 171).

We may regard calcium phosphate ($Ca_3(PO_4)_2$) as composed of two oxides, 3 CaO and P_2O_5. The calcium oxide seems to unite with the sand to form calcium silicate, which fuses to a slag and is drawn off at the bottom:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The phosphoric anhydride (P_2O_5) is reduced by the carbon as follows:

$$2\,P_2O_5 + 10\,C \longrightarrow P_4\uparrow + 10\,CO\uparrow$$

These gaseous products pass off through a pipe, and the phosphorus is condensed under water. After further purification it is cast into sticks.

The electric arc between the electrodes of the furnace supplies the necessary heat. This heat is due to the resistance offered to the electric current, and since the heat is developed in a very restricted area, it is possible to get the high temperatures needed for this process.

332. Properties. When prepared in this way, phosphorus is a white, waxy-looking solid which melts at 44° C. and boils at 287° C. Its most striking property is the low temperature at which it catches fire (35° C.). This necessitates its being kept under water and cut under water, for even the friction of the knife is enough to ignite it. Great care must be taken in handling it (never with the fingers) because the burns are deep and poisonous. It is not soluble in water but dissolves readily in some other liquids, such as carbon disulfide.

When exposed in a dark room *it glows;* that is, it gives out light in spite of the fact that its temperature remains low. Usually, when an object gives out light, we think of it as hot; and in fact most things must be heated to 600° C. or higher before they begin to glow. It is well known that glowworms, lightning bugs, and many phosphorescent sea animals have this power of emitting light without heat. This is called **luminescence.**

333. Red phosphorus. When the **white phosphorus** is heated to about 250° C. in a vessel from which air is excluded, it changes into an allotropic form called **red phosphorus.** This substance is dull red and is somewhat heavier than the white form. It is insoluble in carbon disulfide, is not poisonous, and need not be kept under water. The red phosphorus does not melt but when heated passes directly into a vapor. This vapor shows a gram-molecular weight of about 128 grams, which corresponds to the formula P_4. If the vapor is cooled quickly, the white form is produced, but this very gradually changes at ordinary temperatures into the red.

Still another allotropic form of phosphorus has recently been prepared by Bridgman. By heating white phosphorus to 200° C. and subjecting it to an enormous pressure (1200 kilograms per square centimeter), he obtained **black phosphorus,** which is still heavier then the red.

334. Matches. The easy inflammability of phosphorus has resulted in its being used in the manufacture of matches. The

older process consisted in coating the end of a splint of wood with a paste containing white phosphorus, an oxidizing agent, such as lead dioxide (PbO_2), and glue. The head when dry was dipped in varnish to exclude air. Because the use of white phosphorus in the making of matches led to serious cases of poisoning among the workmen, its use in match factories is prevented in the United States by a heavy tax. A nonpoisonous compound of phosphorus known as **phosphorus sesquisulfide** (P_4S_3) is now substituted. This substance is quite as suitable as white phosphorus. When the match is struck, the friction warms up the sesquisulfide and in the presence of the oxidizing agent it takes fire; the heat of this combustion ignites the wood. To make the head of the match burn more easily, it is usually impregnated with paraffin.

Safety matches are tipped with a mixture of an oxidizing agent, a combustible material, such as antimony trisulfide (Sb_2S_3), and a little powdered glass to increase the friction. The side of the box in which they are contained is coated with a thin layer of red phosphorus, antimony trisulfide, and glue. When the match is rubbed, sufficient heat is produced to ignite a small bit of the red phosphorus in contact with the head of the match, which then takes fire. In safety matches the most combustible material (the red phosphorus) and the oxidizing agent are separated; the match can generally be lighted only when these two constituents are rubbed together. Hence safety matches must be struck on the side of the box.

335. Phosphoric Acid. When phosphorus burns with a free supply of oxygen, a white powder is formed known as **phosphorus pentoxide** (P_2O_5):

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$

The most characteristic property of the pentoxide is its great attraction for water. Since it has no chemical effect upon most gases, the latter may be very thoroughly dried by allowing them to pass through tubes containing phosphorus pentoxide.

When this oxide is dissolved in boiling water, phosphoric acid is formed:

$$P_2O_5 + 3\ H_2O \longrightarrow 2\ H_3PO_4$$

The commercial acid, a thick syrupy liquid of 85 per cent concentration, has been prepared in the past by the action of sulfuric acid on phosphate rock (tricalcium phosphate). A new commercial process (the " thermal " process) has recently been developed by which the phosphate rock is converted into phosphorus by reduction with silica and carbon in a furnace, as explained in section 331. The phosphorus vapor is oxidized to the pentoxide by admitting air, and this is then changed to phosphoric acid by the action of water.

336. Phosphates as fertilizers. Since phosphoric acid is a *tribasic* acid it can form three classes of salts, according as one, two, or three of the hydrogen atoms are replaced by a metal. The rock phosphates of Florida (Fig. 172), Georgia, Tennessee, and the Carolinas are very largely composed of calcium phosphate ($Ca_3(PO_4)_2$). Since this phosphate is almost insoluble in water, it is converted by the action of sulfuric acid into the calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), which is much more soluble:

Fig. 172. Hydraulic mining of phosphate rock in Florida.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow 2\ CaSO_4 + Ca(H_2PO_4)_2$$

The resulting mixture of calcium sulfate and calcium acid phosphate is known as ***superphosphate of lime,*** *which is a fertilizer.*

If the "thermal" process for making phosphoric acid can be operated cheaply enough, the phosphoric acid thus prepared can be used in the preparation of phosphate fertilizers. Such a development seems probable in the near future.

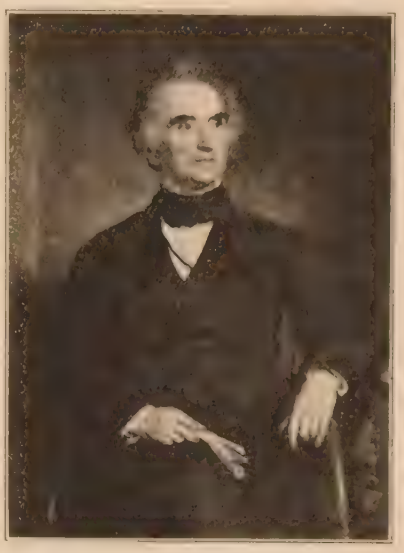


Fig. 173. Justus Liebig (1803–1873). A great German chemist and teacher. Laid the foundations of modern agricultural chemistry.

The composition and proper use of fertilizers is one of the important subjects of investigation in **agricultural chemistry,** which was founded by Liebig (Fig. 173). We have seen that in order to maintain the fertility of the soil *there must be supplied to it* ***three*** *substances:* (1) *nitrogen compounds,* (2) *potassium compounds,* and (3) *soluble phosphates.* Commercial fertilizers are usually a mixture of these three fundamental materials. But the composition of the fertilizer has to be varied to suit the needs of the crop to be raised and the composition of the soil. It frequently happens that soil needs **liming** because it contains too much acid formed from decomposing vegetable matter. Such crops as grains and grass will not thrive on *sour* soil, and so it is *sweetened* by spreading slaked lime ($Ca(OH)_2$) upon it.

337. Trisodium phosphate as a cleanser. In recent years increasing amounts of trisodium phosphate (Na_3PO_4) have been used as a cleaning agent. This substance forms the basis of many cleaning powders that are sold for household use. The value of this chemical as a cleanser depends on the fact that in

water solution it is largely hydrolyzed (§ 286) according to the following equation:

$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH$$

A solution of trisodium phosphate is therefore alkaline and dissolves grease like sodium hydroxide. Since the hydrolysis is only *partial*, the concentration of hydroxyl ions is never as high as in a corresponding sodium hydroxide solution, and the corrosive action of caustic soda (sodium hydroxide) is largely avoided. The hydrolysis of trisodium phosphate is, however, more far-reaching than that of sodium carbonate (Na_2CO_3); and therefore solutions of trisodium phosphate are more alkaline than solutions of sodium carbonate, or washing soda. The relative alkalinities of some common cleansing agents are illustrated in the following table:

	Approx. Grams of OH Ion in a Liter
Sodium hydroxide, 0.25 molar (about 1%)	4.00
Trisodium phosphate, 0.25 molar	0.50
Sodium carbonate, 0.25 molar	0.05
Ammonium hydroxide, 0.25 molar	0.05

Arsenic and Antimony

The next two members of the family, arsenic and antimony, are of minor importance, and we shall consider them but briefly. They look very much like metals, and in their physical properties they show little resemblance to either nitrogen or phosphorus. They behave, however, essentially as nonmetals.

338. Occurrence and preparation. Both elements occur in nature as sulfides. The ore is roasted, forming an oxide, which is then reduced. Most of the natural sulfides contain more or less arsenic; when these ores are oxidized, the sulfur dioxide passes off as a gas, while the arsenic trioxide (As_2O_3) settles as a solid in the flues. The deposit is reduced with carbon:

$$As_2O_3 + 3\,C \longrightarrow 2\,As\uparrow + 3\,CO\uparrow$$

339. Properties and uses. Both elements have a silvery luster; arsenic tarnishes quickly, but antimony does not tarnish. Metallic arsenic is added in very small amounts (about 0.5 per cent) to lead in making small shot. The arsenic lowers the freezing point of the solvent lead and delays its solidification as it drops from the top of the shot tower. It also imparts to the lead the required hardness.

Finely powdered antimony, known as **antimony black,** is used to coat plaster casts in order to give them a dull metallic appearance.

When these elements burn they form oxides, **arsenic trioxide** (As_2O_3) and **antimony trioxide** (Sb_2O_3) respectively. The arsenic trioxide is the "white arsenic" of commerce. It is very poisonous and when mixed with a water solution of a copper salt it furnishes a valuable insecticide known as **Paris green.** The oxides are anhydrides of weak acids, which can be easily oxidized to arsenic acid (H_3AsO_4) and antimonic acid (H_3SbO_4). In these higher acids the elements have the valence of five.

Arsenic and antimony also show some of the characteristic properties of metals in that they form certain compounds which in water solution give a slight concentration of the ions, As^{+++} and Sb^{+++}.

Bismuth

340. Bismuth. The last member of this family is a metal which shows only a few nonmetallic properties. It is not a very important substance. When heated strongly the metal burns, forming a trioxide (Bi_2O_3). This is essentially a basic oxide and forms salts, such as bismuth nitrate ($Bi(NO_3)_3$). If this nitrate is placed in water, a white insoluble **basic** nitrate ($BiONO_3$) is formed, which is used in medicine as "bismuth subnitrate."

341. Useful alloys of antimony and bismuth. Bismuth is used in preparing alloys with very low melting points. For example, **Wood's metal,** which contains bismuth, lead, tin, and cadmium, melts at 60° C., a temperature lower than the melting point of any of the components. Such alloys are used in sprinkler systems. If a fire breaks out in a room

provided with sprinklers plugged with this alloy, the plug (Fig. 174) soon melts and allows the water to gush out and extinguish the fire. These alloys are also valuable materials for safety plugs in steam boilers and for connecting links in devices which automatically close fire doors and curtains.

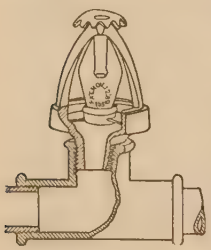


Fig. 174. Fusible plug of sprinkler system.

When antimony is added to lead and tin, the alloy obtained by melting them together is called **type metal**. This has the property of expanding slightly when it solidifies, which makes it useful in type founding. **Babbitt metal** contains the same metals in a different proportion, plus a little copper. It is used to line journal bearings in machinery. In such antifriction alloys the harder particles are pressed into the softer matrix (embedding material) so that a smooth surface is always presented.

SUMMARY OF CHAPTER XXVII

THE PHOSPHORUS FAMILY consists of nitrogen, phosphorus, arsenic, antimony, and bismuth.

PHOSPHORUS is an important constituent of plants and animals. The common allotropic forms are white and red.

White Phosphorus	Red Phosphorus
Melts at 44° C.	Does not melt
Very poisonous	Not poisonous
Low ignition point	High ignition point
Soluble in carbon disulfide	Not soluble
Phosphorescent in air	Not phosphorescent

Red phosphorus and the sulfide of phosphorus are used in the manufacture of matches.

CALCIUM PHOSPHATES are important materials in fertilizer manufacture.

ARSENIC AND ANTIMONY have a physical appearance resembling *metals*. They burn in air, forming oxides which are *acid anhydrides*. They both form certain compounds which give a slight concentration of trivalent positive ions. Arsenic com-

pounds are very poisonous. Antimony is a component of type metal and other alloys.

BISMUTH is a typical metal; it is used in making certain alloys which have a low melting point.

Questions and Problems

1. Name three other elements besides phosphorus which have allotropic forms.

2. Why is red phosphorus more stable than white phosphorus?

3. What is the danger in using ordinary friction matches?

4. Sodium is kept under kerosene, white phosphorus under water. Explain.

5. What characteristics has arsenic which belong to a metal?

6. What essential characteristic has type metal which makes it useful?

7. Name three practical applications for Wood's metal.

8. What three elements are usually found in artificial fertilizers?

9. Calculate the percentage of phosphorus in calcium phosphate ($Ca_3(PO_4)_2$).

10. How much sulfuric acid will be required to treat 1 ton of phosphate rock? Assume the acid is 50% pure acid and the rock is 70% calcium phosphate.

11. Compute the atomic weight of phosphorus from the formula P_2O_5 and the fact that 18.585 grams of phosphorus give 42.584 grams of phosphoric pentoxide.

12. Find the cost of the metals used to make 10 pounds of the fusible metal known as Wood's metal, which consists of 4 parts bismuth, 2 parts lead, 1 part tin, and 1 part cadmium. Assume these prices per lb.: bismuth $2.75; lead 9 cts.; tin 65 cts.; cadmium 60 cts.

Topic for Further Study

Fertilizers. Why does land need to be fertilized? What are the elements that must be supplied in the form of fertilizer? Is there an abundant supply of fertilizer material? What other factors affect crops besides fertilizers? (Slosson's *Creative Chemistry*, Duncan's *Chemistry of Commerce*, *Chemistry in Agriculture*, Howe's *Chemistry in the World's Work*, and pamphlets issued by the State and Federal Agricultural Stations.)

CHAPTER XXVIII

CARBON, COAL, AND FUEL GASES

Carbon, its allotropic forms — diamond and graphite — coal, coke, lampblack, and boneblack — chemical behavior of carbon — coal as fuel — heat units — calorimeter — fuels and smoke — fuel gases: natural, coal, water, and producer — gas burners and flames — acetylene welding.

342. Allotropic forms of carbon. It certainly requires considerable imagination to believe that charcoal, graphite, and diamond are only different forms of one and the same element. But despite their widely different physical properties they are all elementary carbon, and we may prove this experimentally by showing that each of them will burn in oxygen and evolve carbon dioxide as the sole product. Just as in the case of sulfur, we have here two crystalline forms, **diamond** and **graphite,** as well as certain **amorphous,** or noncrystalline, forms, such as charcoal and lampblack. It is possible to change these forms into one another. Charcoal can be converted into graphite by heating it to a very high temperature. It is even possible to make very small diamonds artificially.

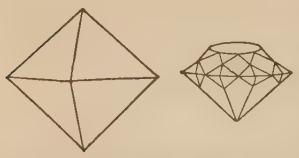


Fig. 175. Diamonds, rough and cut.

343. Diamonds. In certain localities of South Africa, South America, and the East Indies **diamonds** are found in gravel deposits. In their native state they are not at all like the gems which the name suggests. They generally look like ordinary rough stones, hardly transparent, and with little appearance of being crystals. To make them into gems (Fig. 175) they are ground, or "cut," in

such a way that they will reflect light from a number of different faces; that is, "sparkle" in the light.

Diamond is one of the hardest substances known. It can be cut and polished only by other diamonds or by diamond powder. Some diamonds are brownish and even black; these are used for cutting glass and for giving a cutting edge to drills and rock-borers.

344. Graphite. Another form of crystalline carbon is **graphite.** Although it occurs in nature abundantly in certain localities, it is now also manufactured on a large scale from hard coal. Hard coal is a form of impure carbon, which passes into

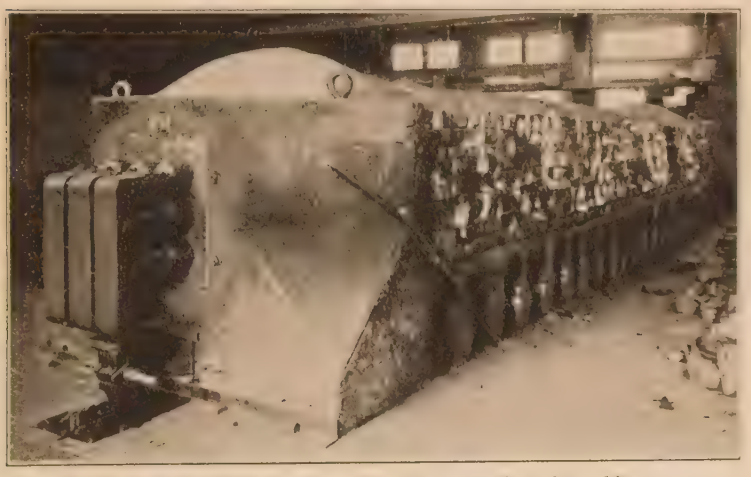


Fig. 176. Electric furnace for the production of graphite.

graphite when it is subjected to a very high temperature out of contact with the air. This high temperature is produced in a so-called electric **resistance furnace.** A powerful electric current passes through a long bed of coal. Since coal is a poor conductor of electricity, its resistance to the electric current produces large quantities of heat, which raises the mass to the desired temperature. The electric current plays no part in the chemical

changes brought about in such a furnace, but merely generates the necessary heat (Fig. 176).

Graphite is a glistening, black substance, which consists of a mass of fine, crystalline, slippery scales. It is soft and greasy and for this reason enters very extensively into the manufacture of lubricants. When mixed with water the suspension is known as **aquadag** and when mixed with oil as **oildag.** It is also used in making stove polishes and paint. Crucibles are often made of it because it will not melt at the highest temperature. It is sometimes called **plumbago,** or **black lead.** " Lead " pencils do not contain lead, but graphite mixed with clay. The hard and soft pencils are obtained by varying the amount of clay.

345. Noncrystalline carbon. The noncrystalline, or **amorphous,** forms of carbon are prepared in many ways. Pure amorphous carbon can be got by heating cane sugar, which is a compound of carbon, hydrogen, and oxygen. On being heated, the hydrogen and oxygen escape as water and leave the amorphous carbon. **Wood charcoal** is another form of amorphous carbon, but it contains a small amount of impurities as ash. It is made by heating wood out of contact with the air, a process which is called **destructive distillation.** Certain volatile materials, such as wood alcohol and acetic acid, are evolved during this treatment. In the older processes for making charcoal these were allowed to escape, but in a modern plant (Fig. 177) they are condensed and used. **Coke** is still another common substance which is essentially amorphous carbon. It is formed from coal in exactly the same way that charcoal is made from wood. Both coke

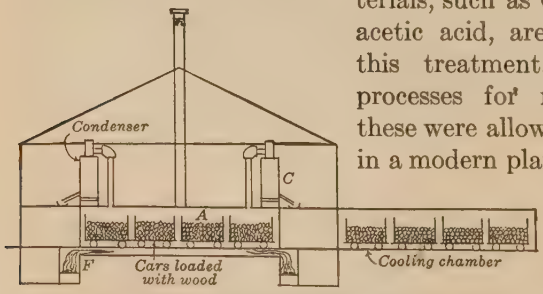


Fig. 177. Modern plant for making wood charcoal.

and charcoal are used as fuels and as reducing agents in metallurgical operations.

The reduction of copper oxide with carbon will illustrate this use. We heat a mixture of black copper oxide and charcoal in a hard-glass test tube (Fig. 178) and lead the gas evolved into limewater. The white precipitate shows carbon dioxide. Metallic copper is left in the tube:

$$2\,CuO + C \longrightarrow 2\,Cu + CO_2\uparrow$$

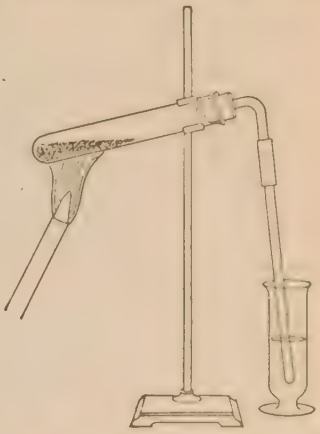


Fig. 178. Reduction of copper oxide by carbon.

We shall mention only a few of the other forms of amorphous carbon. **Lampblack** is made by burning certain oils in a limited supply of air and collecting the soot. **Carbonblack** is similarly prepared by burning natural gas. Both are impure carbon. Large quantities are used in the manufacture of printer's ink, paint, and automobile tires. The charcoal which is made by heating bones without access of air is called **animal charcoal,** or **boneblack,** and is extensively used in decolorizing solutions; for example, in the refining of sugar. Thus we see that coke, charcoal, and boneblack are produced by the destructive distillation of coal, wood, and bones respectively.

346. Coal. The most important variety of amorphous carbon is coal (Fig. 179). The coal we burn to-day was once living vegetation. This has long been buried under beds of sand as the result of certain geological changes which have taken place in the earth's crust, and has been subjected to pressure and fairly high temperatures. In consequence the vegetable material has undergone a partial decomposition, yielding amorphous carbon as the main product. **Anthracite coal** (hard coal) is about 90 per cent carbon, nearly all of which

is in the uncombined state. **Bituminous coal** (soft coal) contains somewhat less carbon ; a considerable part of it is combined

Fig. 179. Mining coal with modern electrical machinery.

with hydrogen, oxygen, nitrogen, and sulfur. Coal is used directly as a fuel and also for the manufacture of coke.

The plant for the production of coke (Fig. 180) consists essentially of the following parts : **iron retorts** or ovens in which the soft coal is heated ; a series of **towers** and **scrubbers** through

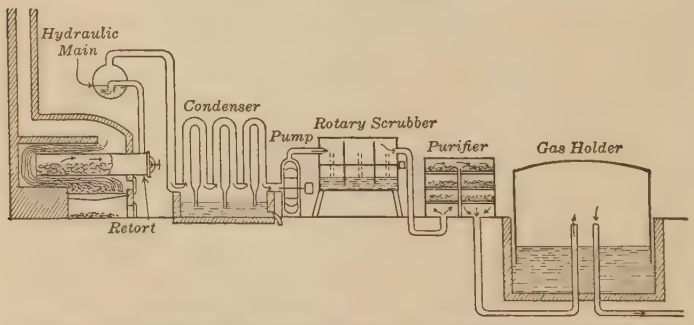


Fig. 180. Diagram of a plant for making coal gas and its by-products.

which the gases pass in order to remove heavy, tarry material (coal tar), ammonia gas, and hydrogen sulfide; a gas **holder** to collect the purified coal gas. The coke is left in the retorts. **Coal tar** and ammonia, as well as the coal gas and the coke, are of great commercial value (Fig. 181).

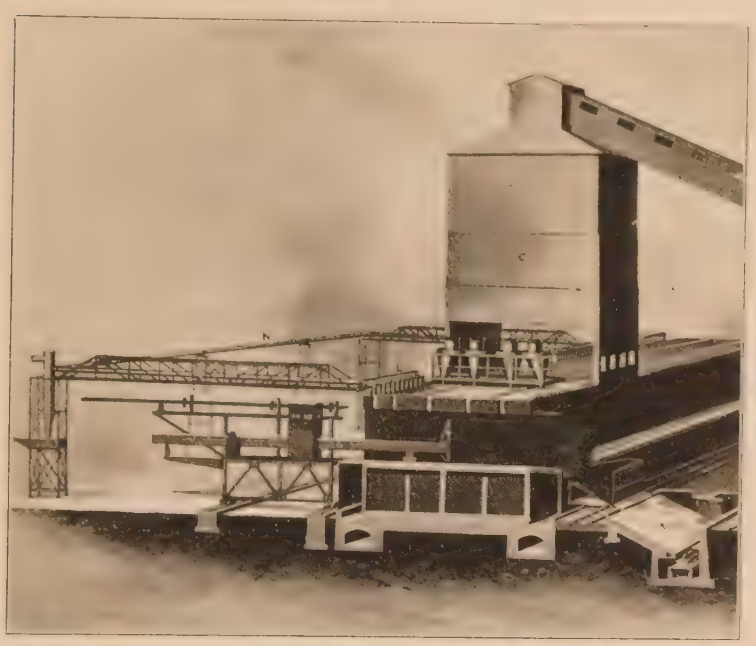


Fig. 181. Diagrammatic view of a by-product coke oven showing the coke being removed from one of the ovens.

347. Chemical behavior of carbon. None of the forms of carbon react with either bases or acids. They do not dissolve in ordinary solvents, although melted iron does dissolve carbon to a certain extent. At ordinary temperatures *all forms of carbon are very inert;* but at high temperatures they all burn, forming carbon dioxide, or, in a limited supply of oxygen, carbon monoxide. At high temperatures carbon acts as a reducing agent and thus removes oxygen from the oxides of many

metals. This is essentially the process of producing metals from their ores.

348. Coal as a fuel. Carbon in the form of coal is the source of nearly all the energy which is used to run our factories and to keep us warm in winter. But carbon alone is not sufficient; we must burn it, and in order to burn it we must have oxygen. Thus, both carbon and oxygen are necessary for the production of the energy which is set free when they combine. When we buy a ton of coal, we are not especially interested in the gases which go up the chimney or in the ashes left behind, but we are interested in the **energy** produced.

Heat is the form of energy with which we are most familiar; but heat, light, and electricity are all forms of energy. The energy of anything is its **capacity for doing work.** *Energy*, like matter, *may be transformed, but it can never be created or destroyed.* This has been called the LAW OF CONSERVATION OF ENERGY. Since energy has no weight, it must be measured by some effect which it produces.

349. How we measure heat. Experiments show that if one pound of hard coal could be completely burned, and if all the heat generated in this process could be used to heat water, the temperature of one ton of water would be raised about 7° F. Engineers reckon the heat value of fuel in units, each of which *is equal to the heat required to raise the temperature of one pound of water one degree Fahrenheit.* This heat unit is called the **British thermal unit** and is written **B.t.u.** For example, the heat value of a pound of coal varies from 11,000 to 16,000 B.t.u.

The heat unit used in Europe and in all physical and chemical laboratories is a metric unit called the **gram calorie.** *A gram calorie is the heat required to raise the temperature of one gram of water one degree centigrade.* We also have the kilogram calorie, which is equivalent to 1000 gram calories.

350. Calorimeter. The apparatus which is used to determine the heat value of a fuel is called a **calorimeter** (Fig. 182).

The apparatus consists of a strong steel cup, or bomb, with a tightly fitting screw cap. A sample of coal (about 1 g.) is weighed and placed in the little tray inside the steel cup, and a piece of platinum wire is connected to the electrodes of the bomb and allowed to dip into the coal. Then the cap is screwed into place, and oxygen is forced in under considerable pressure. The cup is now placed in a can of water which is surrounded by air space and more water, and the outside container is covered with felt. The apparatus is provided with a thermometer reading to 0.001° C. and has a mechanical stirrer. The coal is fired by sending an electric current through the platinum wire. The rise of temperature is noted. From the weight of the water and its rise in temperature (corrected), the heat value of the coal can be computed.

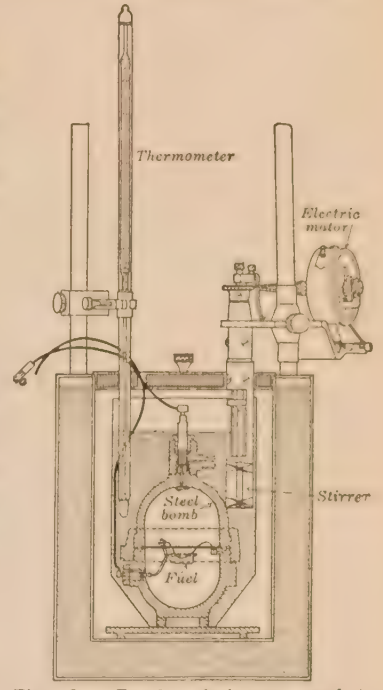


Fig. 182. Bomb calorimeter used to measure the heat value of coal.

Another type of fuel calorimeter, known as Parr's Peroxide Bomb, does not use oxygen gas as just described. Sodium peroxide is mixed with the fuel sample and ignited in the bomb. This apparatus is less expensive and sufficiently accurate for approximate determinations.

351. Fuels and smoke. Coal, coke, wood, and charcoal are common forms of **solid fuel.** When heated sufficiently, these substances burn, producing carbon monoxide and carbon dioxide. This chemical reaction is called **exothermic** because *heat is liberated.* When 12 grams of carbon (its atomic weight) are burned to carbon dioxide, the amount of heat generated is

96,480 calories. Since this heat is an important result of the reaction, we may express it as follows:

$$C + O_2 \longrightarrow CO_2 + 96{,}480 \text{ cal.}$$

In large furnaces much carbon monoxide and unconsumed coal in the form of fine particles may escape if insufficient air is supplied or if the furnace is not properly constructed. This unconsumed coal is responsible for the **smoke** which has become such a serious public nuisance in many of our cities where large quantities of soft coal are burned. The smoke involves in addition an enormous waste of fuel. By properly designing the fire box of the furnace (Fig. 183) and by regulating the supply of fuel and air, complete combustion will ensue, and no smoke will be formed. This is economical from the point of view of the factory, and is very desirable for those who inhabit the surrounding country.

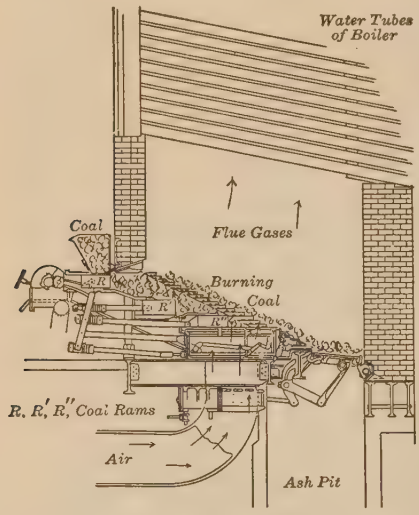


Fig. 183. Boiler with underfeed automatic stoker, which gives smokeless combustion.

352. Gaseous fuels. In certain parts of the United States a mixture of gases issues from the ground which is called **natural gas.** The chief constituent of this gas is methane (CH_4). Natural gas burns with a luminous flame; it is used for lighting and heating purposes in many of our cities, and as fuel in many industries. The gas obtained in the destructive distillation of coal is called **coal gas.** It also contains methane and in addition

hydrogen, carbon monoxide, and some complex compounds of carbon. As it burns with a luminous flame, it is used for lighting purposes in many cities. **Water gas** is a mixture of hydrogen and carbon monoxide produced by passing steam over red-hot coal. The reaction is:

$$H_2O + C \longrightarrow CO + H_2 - 26{,}990 \text{ cal.}$$

It will be noticed that in this reaction heat is absorbed; that is, heat must be supplied to keep it going. Such a reaction is called **endothermic.**

The process of making water gas (Fig. 184) is carried out by alternately allowing a mass of coal to burn in air until it becomes red-hot,

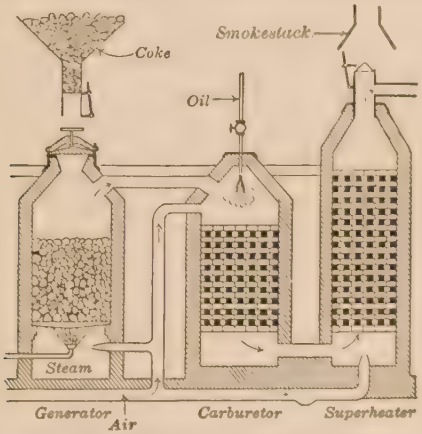


Fig. 184. Diagram of a water-gas plant.

and then shutting off the air and blowing in steam; the water gas which is formed in the second part of the process is collected. When the temperature has fallen too low, the steam is shut off and air again admitted. Since hydrogen and carbon monoxide both burn with non-luminous flames, water gas must be treated before it can be used for lighting purposes. This is done by adding certain volatile petroleum oils. **The process is called enriching.**

There is another gas which is used in many metallurgical operations and as a fuel for gas engines; this is called **producer gas.** It is made by

forcing air through a very deep coal fire in the generator (Fig. 185). The resulting gas mixture contains all the nitrogen of the air, but all the oxygen has combined with carbon to form carbon monoxide. Often a little steam is introduced with the air and is reduced as in the making of water gas. If made in this way, producer gas is composed mainly of nitrogen, carbon monoxide, and hydrogen.

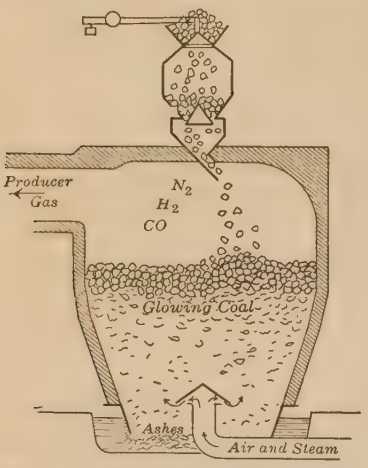


Fig. 185. Diagram of a producer-gas plant.

The accompanying diagram (Fig. 186) illustrates the approximate composition of these various fuel gases by volume.

353. Gas burners and flames. When gas burns in the ordinary **fishtail burner,** it is spread out in a thin sheet by the tip so that sufficient air is brought into contact with the gas to burn all of the carbon. In the flame itself some of the complex carbon compounds are broken down into free carbon by the high temperature. This

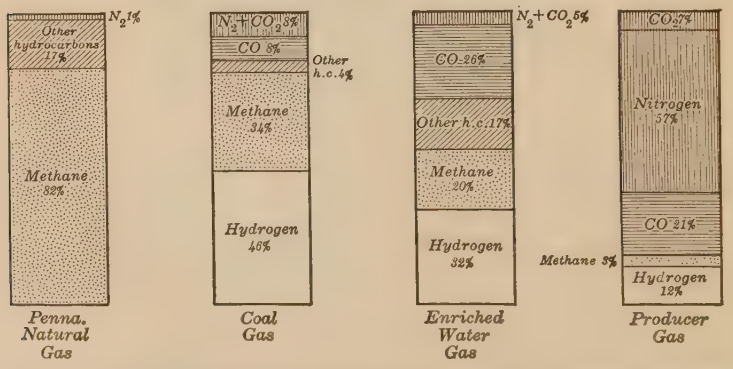


Fig. 186. Diagram showing the approximate composition of various fuel gases.

free carbon is heated white-hot by the combustion which is going on, and it is these particles of incandescent carbon which give the flame its illuminating power. Water gas contains no such carbon compounds and must therefore be enriched. Figure 187 shows the structure of this type of flame. It will be noticed that there are several distinct zones. The luminous zone is full of particles of white-hot carbon, which on passing to the outer zone are completely consumed, forming carbon dioxide; the heat given off in this combustion keeps the flame at the necessary temperature.

Fig. 187. Parts of a gas-jet flame.

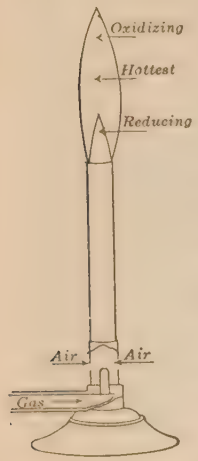


Fig. 188. Bunsen burner and flame.

In a **Bunsen burner** (Fig. 188) we admit air into the interior of the flame. This cools down the flame so much that the temperature is not high enough to decompose the complex carbon compounds into free carbon; the flame is therefore nonluminous. The burners on a gas range (Fig. 189) are modified Bunsen burners, so arranged as to give a large number of small blue flames.

354. Uses of acetylene. Acetylene (C_2H_2) is a gas produced by the action of water on calcium carbide, which is made from carbon and lime in an electric furnace.

Fig. 189. Burner used on a gas range.

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2\uparrow$$

It can either be generated as required, or can be conveniently dissolved in a liquid known as acetone in a tank under pressure. Acetylene will burn with a very luminous flame in an especially constructed burner which admits air. It is used to a limited extent for illuminating purposes. If oxygen is blown through such a flame, complete combustion of the acetylene takes place,

Fig. 190. Cutting steel plate with oxyacetylene torch.

and we obtain a very hot, nonluminous flame. This flame is one of the hottest known and is used extensively because it will easily melt iron and other metals.

Acetylene is an endothermic compound, and when it decomposes heat is generated, as shown in the following equation:

$$C_2H_2 \longrightarrow 2\,C + H_2 + 49{,}300 \text{ cal.}$$

In the acetylene flame the heat of combustion of the carbon and hydrogen is added to this heat of decomposition:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 603{,}000 \text{ cal.}$$

With the right mixture of oxygen and acetylene, it is possible to get a temperature of about 2700° C. The **oxyacetylene torch,** which is very much like the oxyhydrogen blowpipe, cuts steel by melting and burning it. The tip of the flame when drawn slowly over the metal melts it at the point of contact, and the excess oxygen burns the molten iron to iron oxide, which is blown off as a shower of sparks. It is especially useful in dismantling steel structures (Fig. 190). Pieces of iron and other metals may be welded, that is, joined together, by heating them until they melt and then allowing the molten metal to fuse together.

SUMMARY OF CHAPTER XXVIII

THE THREE ALLOTROPIC FORMS of carbon are *diamond*, *graphite*, and *amorphous carbon.* They have different physical properties, but all yield carbon dioxide when burned in sufficient oxygen.

CARBON IS INERT at ordinary temperatures but burns at high temperatures. It is a reducing agent. It reacts with lime to form calcium carbide when heated in an electric furnace.

USES OF CARBON in different forms are —

Diamond: gem and abrasive;

Graphite: lead pencils, lubricant, crucibles, and electrodes;

Coal: fuel and in manufacture of illuminating gas and coke;

Coke: ore reducer, fuel, and in making water gas;

Carbonblack, Lampblack: printer's ink, paint, and automobile tires;

Boneblack: decolorizing sugar and oils.

MOST IMPORTANT FUEL IS COAL. Heat is measured in *calories.* A calorie is the heat required to raise one gram of water one degree centigrade. Engineers' heat unit is B.t.u. (British thermal unit).

CHEMICAL REACTIONS which give out heat are called *exothermic;* a few reactions absorb heat and are called *endothermic.*

FUELS are substances which burn in air. The reaction is strongly exothermic; we carry out this reaction because we want the heat evolved.

SOLID FUELS are coal, coke, wood, and charcoal.

FUEL GASES include natural gas, coal gas, water gas, and producer gas. Fuel gases which contain hydrocarbons burn with a luminous flame because carbon is set free.

ACETYLENE is produced from calcium carbide. The oxy-acetylene flame is extremely hot and is used for cutting and welding metals.

Questions and Problems

1. What is the easiest way to show the presence of carbon in a compound?

2. What is the most useful form of carbon? Explain. What is the most expensive form? Why?

3. What are the by-products in the coal-gas industry?

4. How do we measure the fuel value of coal?

5. What are characteristics of a good fuel?

6. What characteristics of graphite make it useful (*a*) as a paint? (*b*) as a lubricant?

7. How would you prove that carbon dioxide and water are formed when illuminating gas burns?

8. Why is it desirable to remove the sulfur compounds from illuminating gas?

9. Why is producer gas not used for illuminating purposes?

10. Which fuel gas is richest in hydrogen? in methane? in carbon monoxide? (Examine diagram.)

11. Why is not the flame used in a gas range smoky?

12. How is the burner in a gas range different from the Bunsen burner used in the laboratory?

13. For what especial purposes is the acetylene lamp adapted?

14. How many tons of oxygen are required to burn completely one ton of coal which is 90% carbon?

15. How many tons of carbon dioxide are produced in Problem 14?

16. How many grams of carbon will be required to reduce 10 g. of copper oxide to metallic copper?

17. Write the equation for the complete combustion of acetylene.

18. How many liters of air are required to burn 1 liter of acetylene?

19. How many gram calories of heat are generated when a kilogram of soft coal (80% C.) is burned to carbon dioxide?

20. To determine the fuel value of a coal, a 1-gram sample was burned in a bomb calorimeter containing 1.5 liters of water. The temperature of the water was raised 5.05° C. Compute the fuel value (*a*) in gram calories per gram and (*b*) in B.t.u. per pound.

Topic for Further Study

Fuel and power. If possible, see in operation furnaces or stoves burning gas, oil, and coal mechanically stoked. What are some of the relative merits of each fuel? In certain parts of the country only anthracite coal is used in the homes; why? The iron blast furnace requires anthracite coal or coke as a fuel; the glass industry requires gas or oil. Explain. (Cressy's *Discoveries and Inventions*, Howe's *Chemistry in the World's Work*, and Findlay's *Chemistry in the Service of Mankind*.)

CHAPTER XXIX

ALCOHOL AND GASOLINE

Organic chemistry. Alcohol, preparation, properties, and uses — denatured alcohol, methanol — ether. Hydrocarbons — gasoline — carbon tetrachloride and chloroform — aldehydes — acetic acid.

355. Organic chemistry. The element carbon forms so many compounds of great importance that a separate branch of chemistry is devoted to their study. This subject is known as **organic chemistry** in contrast to **inorganic chemistry**, which deals with all the compounds of the other elements. There are over 200,000 organic compounds already known, and new ones are being discovered every day. In a great many of these compounds carbon is combined with only a few other elements — often only with hydrogen. How can so many compounds of one element exist? The reason is that carbon atoms can form chains by uniting with each other, and these chains may contain from 2 to at least 60 atoms. We shall see that petroleum is a very complex mixture of such compounds of hydrogen and carbon.

356. Ethyl alcohol. One of the simplest and most important organic compounds is ethyl alcohol (C_2H_5OH). This substance is usually spoken of as "grain alcohol," or simply "alcohol." It is the product obtained from the fermentation of sugars, a chemical process brought about by the presence of small living plants, of which yeast is a common example. The other product of the fermentation is carbon dioxide:

$$\underset{\text{sugar}}{C_6H_{12}O_6} \longrightarrow 2\ \underset{\text{alcohol}}{C_2H_5OH} + 2\ \underset{\text{carbon dioxide}}{CO_2}\uparrow$$

The action of the yeast on the sugar solution has been shown to be due to a catalyst which is produced in the living yeast cell as it grows. Such catalysts which are formed in nature are called **enzymes**. They have not yet been isolated in a pure state and we are still ignorant of their chemical nature. Almost all

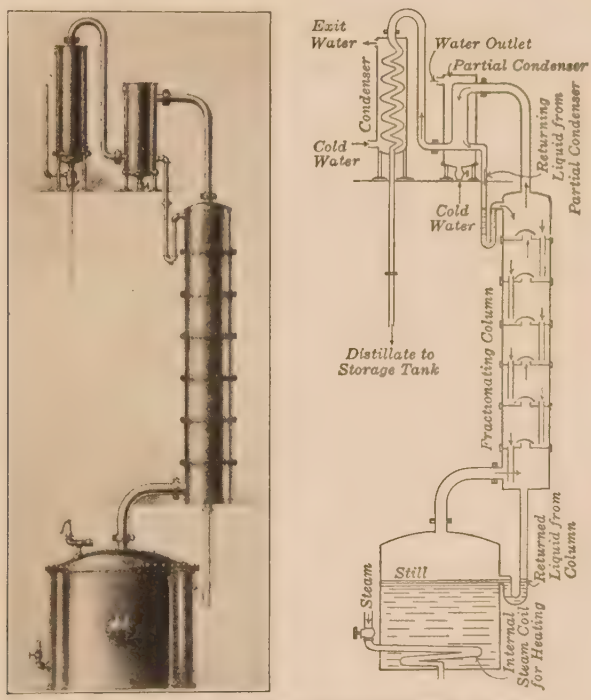


Fig. 191. Commercial still with fractionating column.

the complicated chemical changes which occur in plants and animals are brought about by enzymes.

When a mixture of alcohol and water is distilled, the liquid begins to boil at about 78° C. As the process continues, the boiling point rises until it reaches 100° C., the boiling point of water. If the distillate (what is distilled over) is separated

into **fractions** according to the temperature, the first fraction collected contains a large percentage of alcohol, while the fractions collected during the latter part of the process will be mainly water. On a large scale the distillation is carried out in an apparatus having a tall **fractionating column** (Fig. 191) and partial condenser. The water vapor is condensed in the fractionating column and partial condenser, and returns to the still; the more volatile alcohol passes on until it reaches the total condenser. The distillate is 95 per cent alcohol, and the liquid returning to the still is largely water. This process is called **fractional distillation.**

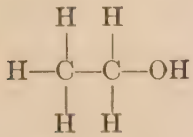
357. Properties and uses of alcohol. Pure alcohol is a colorless liquid boiling at 78° C.; it is inflammable and is used to some extent as a fuel. It usually contains a small amount of water, which cannot be removed by distillation. If boiled with lime, this water is removed and **absolute alcohol** is formed. It mixes with water in all proportions but is not ionized in aqueous solution; it does not interact with dilute acids, bases, or salts. It is an excellent solvent, dissolving many substances which are only slightly soluble in water. It is the solvent used in making varnishes for wood and lacquers for metal, as well as in the manufacture of celluloid, collodion, and artificial silk. **Tinctures** are alcoholic solutions of medicinal substances. Many perfumes and flavors (extracts) are alcoholic solutions.

358. Industrial alcohol (denatured alcohol). The sale of pure ethyl alcohol is strictly regulated by the laws of the United States. Alcohol which has been rendered unfit for beverage purposes may be sold freely and is tax-free. This is called completely denatured alcohol and usually contains the poisonous methyl alcohol (see below) and also some evil smelling substance. The use of especially denatured alcohols for industrial purposes is permitted under governmental control.

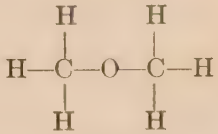
Industrial alcohol is prepared either by the fermentation of the residues from cane-sugar refining (molasses), or from starchy

materials such as potatoes or grain. Molasses may be fermented directly, producing alcohol; but if starch is the starting point, this is first converted to sugar by the action of an enzyme (diastase) present in sprouting barley (§ 377).

359. Formula of ethyl alcohol. The formula of ethyl alcohol might be written C_2H_6O, which tells us that there are 2 carbon atoms, 6 hydrogen atoms, and 1 oxygen atom. This is called an **empirical formula** and states the facts derived from the percentage composition and molecular weight of the substance. It would be sufficient for most of the inorganic compounds which we have thus far studied. But it is inadequate in organic chemistry; for *it often happens that there are several compounds which have the same empirical formula.* Such substances are called **isomers.** For example, there is another substance, called methyl ether, which also has the formula C_2H_6O but which is a gas having totally different properties from ethyl alcohol. The difference between these two isomers must lie in the way their atoms are joined together. We are thus led to inquire how the atoms are linked and to show this linkage in our formulas. Accordingly we write them graphically as follows:



ethyl alcohol



methyl ether

Since these formulas show how every atom in the molecule is joined to every other one, they are called **structural** formulas. We usually condense such a formula as that of alcohol and write it C_2H_5OH. The number of isomers in organic chemistry is very large, and it is because of this fact that only structural formulas have a real significance for the organic chemist.

We cannot here consider how these structural formulas are derived; it is enough to say that they rest on a mass of experi-

mental evidence. They tell the trained chemist how a given substance will probably react, because he knows that certain linkages represent certain reactions. It has been found that in organic compounds carbon always has the valence 4. This point is useful in remembering and writing structural formulas.

360. Methanol. Another well-known substance is **methanol, or wood alcohol** (**methyl alcohol**), which has the formula CH_3OH. It resembles ethyl alcohol in many of its properties and is used as a solvent and as an agent for denaturing ethyl alcohol *since it is very poisonous.* It is prepared either by the destructive distillation of wood or synthetically from carbon monoxide by a recently developed process. A mixture of carbon monoxide and hydrogen (water gas) under high pressure and at an elevated temperature is passed over a catalytic agent. The reaction represented by the following equation takes place:

$$CO + 2\,H_2 \longrightarrow CH_3OH$$

This new catalytic process is very cheap and may in a short time entirely supplant the destructive distillation of wood.

361. Other alcohols. The term alcohol really applies to a class of substances although it is commonly applied to one particular member of the class — ethyl alcohol. The following table shows the names and formulas of a number of alcohols, which are arranged in a series with an increasing number of carbon atoms. Such a series is called an **homologous series.** Each member differs from the one above or below it by two hydrogen atoms and one carbon atom (CH_2). All members of such a series have much the same chemical properties, but their physical properties differ gradually as we go up the series.

Name	Formula	Molecular Weight	Boiling Point C.
Methyl alcohol	CH_3OH	32	64.7°
Ethyl alcohol	C_2H_5OH	46	78.3°
Propyl alcohol	C_3H_7OH	60	97.2°
Butyl alcohol	C_4H_9OH	74	117.5°
Amyl alcohol	$C_5H_{11}OH$	88	137.0°

362. Ether. When ethyl alcohol is treated with sulfuric acid under certain conditions, ethyl ether and water are formed. Ethyl ether, or as it is usually called, ether, has the structure represented by the formula $(C_2H_5)_2O$ and may be regarded as ethyl oxide. The equation for its formation is as follows:

$$\underset{\text{ethyl alcohol}}{2\,C_2H_5OH} \longrightarrow \underset{\text{ethyl ether}}{(C_2H_5)_2O} + H_2O$$

It will be noticed that in ether we have two ethyl groups (C_2H_5) joined together by an oxygen atom. It is a colorless liquid boiling at 35° C. It is prepared on a large scale and is used extensively as a solvent and as an anæsthetic. It produces unconsciousness when inhaled and has been used for a number of years in surgical operations.

363. Petroleum, a mixture of hydrocarbons. The natural oil, petroleum, is a mixture of compounds of carbon and hydrogen, called **hydrocarbons.** Practically nothing is known about the individual components of this complex mixture. The chemists have been able to isolate but a few of the constituents in a pure state. Our knowledge of the individual hydrocarbons is a result of the preparation of the pure substances in the laboratory. There are several hundred of these compounds of carbon and hydrogen known, and they may be grouped into series according to their composition. One group is called the **paraffin series,** of which only the first six are given in the table on page 346.

HYDROCARBONS OF THE PARAFFIN SERIES

NAME	FORMULA	MOLECULAR WEIGHT	BOILING POINT C.
Methane	CH_4	16	− 160°
Ethane	C_2H_6	30	− 93°
Propane	C_3H_8	44	− 45°
Butane	C_4H_{10}	58	+ 1°
Pentane	C_5H_{12}	72	36°
Hexane	C_6H_{14}	86	71°

It will be noticed that the series starts with **methane,** the principal component in natural gas, and that the difference between each two successive members in the list is CH_2. It will also be noticed that the number of hydrogen atoms is twice the number of carbon atoms plus two. This fact can be expressed in the general formula C_nH_{2n+2}. The members of this series have higher boiling points as the molecules become larger; so that the first four are gases, the next ten are liquids under ordinary conditions, and above that they are solids. Members of this series have been studied at least as far as hexacontane ($C_{60}H_{122}$). Pennsylvania petroleum is probably composed chiefly of members of this series.

But even this long succession of compounds does not include all the hydrocarbons. Ordinary coal gas owes its luminosity to ethylene (C_2H_4), which is the first member of another series with the general formula C_nH_{2n}. There is yet another group which begins with acetylene (C_2H_2) and has the general formula C_nH_{2n-2}. *All these hydrocarbons are mutually soluble* so that mixtures can be made in any proportion.

It will be seen on comparing the above table with that of the homologous series of alcohols that the two series are closely related. One may regard each alcohol as derived from the corresponding hydrocarbons by removing one hydrogen atom and inserting an hydroxyl group; thus, ethane C_2H_6 and ethyl alcohol C_2H_5OH. Such a process cannot be carried out usually, but the reverse process (replacement of hydroxyl by hydrogen) is possible in several ways and is used in preparing hydrocarbons in the laboratory.

364. Refining of petroleum. In many parts of the United States and in some other countries, petroleum occurs in large

Fig. 192. Derricks of oil wells in Texas.

quantities underneath the surface of the earth. The crude oil is pumped from wells (Fig. 192). Some of it is used directly as a fuel and is called crude burning oil. The greater portion is sent through long pipe lines to the seaboard, where it is refined. This process of refining consists in distilling the substance and then removing certain ill-smelling and tarry materials.

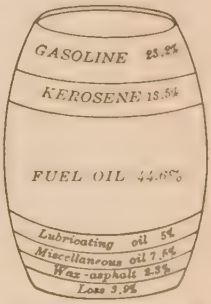


Fig. 193. What comes from a barrel of crude oil.

The distillation is carried out so that different portions which boil at different temperatures are collected separately. The lower boiling fraction (between 70° and 200° C.) is called **gasoline** and is used extensively for automobiles and gas engines. The next portion (boiling between 200° and 300° C.) is called **kerosene** and is used as a burning oil (Fig. 193). It will not take fire directly, but if allowed to moisten a wick in a suitable lamp will burn with a pleasant, luminous flame.

Certain kinds of crude petroleum yield on distillation high-boiling oils (**lubricating oils**) and a solid, waxlike material, **paraffin.** Such oils are said to have a "paraffin base." Other varieties of petroleum do not give lubricating oils and paraffin but a thick, black pitch, which is used in roofing and paving (Fig. 194); such oils are called "asphaltic." Pennsylvania petroleum has a paraffin base; Mexican and Californian oils are for the most part asphaltic. "Liquid petrolatum," or "mineral oil," is a carefully refined high-boiling distillate. It is widely used as a laxative.

Fig. 194. Applying tar to roads.

Oils derived from petroleum are used very extensively as fuel. When they burn, carbon dioxide and water are produced. They are to a small extent burned with the aid of a wick, as in the case of kerosene. For the most part they are blown out from a nozzle in the form of a fine spray mixed with air or steam. This spray is ignited and gives a very long, hot flame. Locomotives and steamships are sometimes fired with crude oil. Oil is also used as a fuel in a number of manufacturing processes, and to some extent as a substitute for coal in heating houses.

365. Gasoline. Of all the products obtained from petroleum, gasoline is the most valuable. Indeed, the production of this cheap liquid fuel has made possible the internal combustion engine and the automobile. The automobile engine is a device for getting power from the explosion of a mixture of air and hydrocarbon vapors. Only relatively volatile hydrocarbons can be employed, as they must be conveyed into the cylinder from the carburetor in a stream of air (partially as vapor, partially as fine drops). The usual grade of gasoline boils between about 60° and 222° C. It is separated from crude oil by fractional distillation (Fig. 195). The larger molecules of the more complex hydrocarbons are not volatile enough to be used directly. They may be turned in part into gasoline by a process called "**cracking.**" This process consists in heating

high-boiling residues from the gasoline-refining process to 500° under pressure. At this temperature the more complicated molecules decompose into simpler substances, which have a lower boiling point and can therefore be used as gasoline.

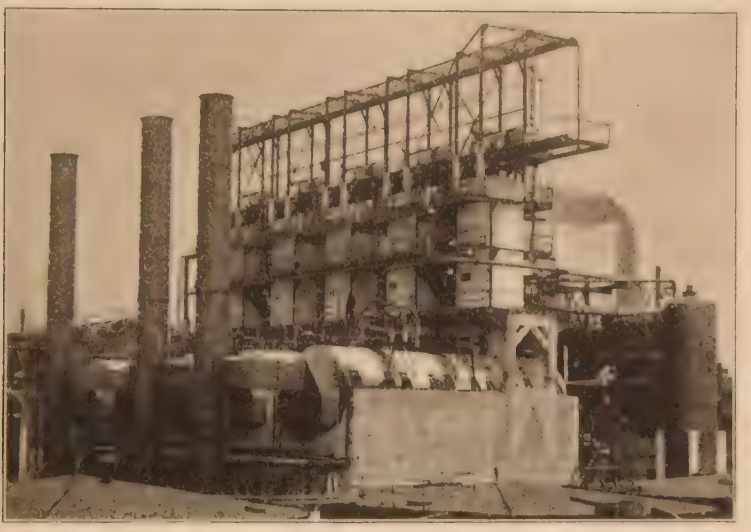


Fig. 195. Plant for making gasoline by fractional distillation of crude oil.

Considerable gasoline is also obtained by recovering from natural gas some of the vapors which often accompany it as it issues from the earth.

366. What goes on in the cylinder. The automobile cylinder is a vessel in which we carry out a chemical reaction with the production of a great deal of heat. This heat produces mechanical energy by expanding the gases produced in the reaction, according to the familiar Law of Charles. We might assume an average composition of gasoline as represented by the formula C_8H_{18}. If this is the case, we can write the reaction for what goes on in the cylinder as follows:

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

Applying the law of combining volumes we see that 27 volumes of the reacting substances give 34 volumes of products — not much change. However, in this reaction a great deal of heat is evolved, and the temperature of the products is probably raised to about 1500° C., expanding the gaseous products enormously. *This heat is the basis of our motive force.*

367. Chemical calculations applied. If we calculate in the usual way the weights of gasoline and air in the reaction, we see that it requires about 15 pounds of air to burn one pound of gasoline. Every mixture of a combustible substance and air has a definite *explosive range.* In the case of gasoline and air, this varies from about $1\frac{1}{2}$ to 6 per cent of gasoline by weight. This is surprisingly little gasoline. If we have more gasoline in our air than this, the mixture will not explode. Our carburetors are designed so that the cylinder will receive a mixture containing the correct proportions of gasoline and air. Unfortunately this ratio will depend upon the vapor pressure of the gasoline, which changes rapidly with the temperature. To make sure of always getting the right mixture, the carburetor must be adjusted if considerable temperature changes occur.

Chemistry of the carburetor. It is easy to show by a simple experiment some of the principles involved in the construction of a carbu-

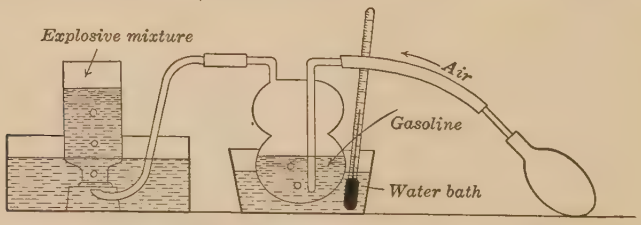


Fig. 196. Effect of temperature on a carburetor.

retor (Fig. 196). The gasoline is contained in a bottle and kept in a water bath at the desired temperature. Air is blown through the bottle and collected in glass cylinders over water in a pneumatic trough.

It is found with ordinary gasoline that at a temperature of 25° C. it is necessary to mix this air saturated with gasoline with about three volumes of fresh air in order to obtain an explosive mixture. At a temperature only 10° lower (15°), a mixture of equal volumes will explode. This shows the marked effect of a few degrees change in temperature.

368. Anti-knock remedies. The explosion of gasoline in the cylinder sometimes proceeds too violently and the engine is said to "knock." It has been found that a small amount of a volatile lead compound, lead tetraethyl ($Pb(C_2H_5)_4$), prevents this. Gasoline containing this compound has been called **"ethyl gas."** It may be used to advantage in engines with very high compression, which are the more efficient. In these untreated gasoline always "knocks" very badly. It has been found, also, that certain hydrocarbons decrease the "knocking" if present in considerable amounts. For this reason gasoline from certain fields and prepared by certain "cracking processes" appears to have superior anti-knocking properties.

369. Carbon tetrachloride and chloroform. If we remove one or more of the hydrogen atoms of a hydrocarbon and put in place of it another atom, we obtain what are called substitution products. Chlorine reacts with methane explosively and forms **substitution products.** If we replace all four hydrogen atoms in methane with chlorine, we obtain a compound called **carbon tetrachloride** (CCl_4). As a matter of fact, the reaction between chlorine and methane is very hard to control, and therefore carbon tetrachloride is actually prepared industrially by another reaction. Carbon disulfide (CS_2) readily reacts with chlorine, forming sulfur chloride and carbon tetrachloride; the two liquids can be separated by distillation:

$$\underset{\text{carbon disulfide}}{CS_2} + 3\,\underset{\text{chlorine}}{Cl_2} \longrightarrow \underset{\text{sulfur chloride}}{S_2Cl_2} + \underset{\text{carbon tetrachloride}}{CCl_4}$$

Carbon tetrachloride is a heavy, colorless liquid boiling at 79° C. and has an odor not unlike that of chloroform. It readily dissolves greases, gums, and resins. As a noncombustible solvent

it finds a wide use in technical operations. It forms the basis of many cleaning fluids. It is the main part of the liquid used in certain small fire extinguishers (Fig. 197). When squirted on the fire it forms a very heavy vapor, which hangs over the burning material, excluding the air and thus extinguishing the flames. It is particularly valuable in putting out burning oil, since such fires cannot be extinguished by water; for oil simply floats on the water and continues to burn.

Fig. 197. "Pyrene" fire extinguisher.

Carbon tetrachloride can be reduced to a substance called **chloroform** ($CHCl_3$):

$$\underset{\text{carbon tetrachloride}}{CCl_4} + \underset{\text{nascent hydrogen}}{2\,[H]} \longrightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{hydrogen chloride}}{HCl}$$

Chloroform can also be prepared by the action of bleaching powder on ethyl alcohol. It is a sweet-smelling, volatile liquid, which finds certain uses as a solvent and as an anæsthetic. It is not so safe an anæsthetic as ether and is employed only in special cases.

Iodoform (CHI_3) is a yellow solid with a characteristic odor. It is used as an antiseptic.

370. Aldehydes. Methyl alcohol can be oxidized to form a substance called formaldehyde (HCHO):

$$\underset{\text{methyl alcohol}}{CH_3OH} + [O] \longrightarrow \underset{\text{formaldehyde}}{HCHO} + H_2O$$

If we write out this formula in full, we see that the oxygen atom has two bonds linking it to the carbon atom. The group

—C=O is the characteristic of a whole class of compounds known as **aldehydes**.

371. **Formaldehyde** is a gas with a penetrating odor, which causes the eyes to smart. It is used in water solution as a disinfectant and an

antiseptic. The 40 per cent solution is sold under the name **formalin**. A solid compound called paraformaldehyde, when heated, breaks down to give the gas. This substance is often sold as a candle (Fig. 198), which can be lighted in a room for disinfection.

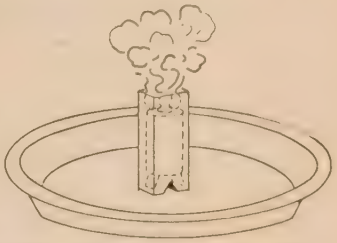
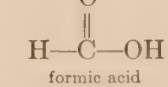


Fig. 198. Formaldehyde candle.

A substance called **Bakelite** somewhat resembling hard rubber is made by the interaction of formaldehyde and phenol (carbolic acid) from coal tar. It is used for the manufacture of such articles as pipe stems, buttons, umbrella handles, phonograph records, and for insulation in electric machinery.

372. Acids. Formaldehyde can be further oxidized to a liquid called **formic acid** (HCOOH). The structural formula shows a doubly linked oxygen atom connected with the carbon atom, and also a hydroxyl group; thus:



formic acid

This combination (COOH) is called the **carboxyl group** and is characteristic of a class of organic substances known as **acids**. They are obtained by oxidizing the corresponding alcohols. There are a number of series of acids; formic acid is the lowest member of a series called the fatty acids, the lower members of which are liquids and the higher members solids. They are all monobasic and form salts on neutralization. Two of the higher acids which are solids, palmitic ($C_{15}H_{31}COOH$) and stearic ($C_{17}H_{35}COOH$), are derived from fats; hence the name of the series.

Acetic acid (CH_3COOH) is the most important lower member of this series. It can be prepared in the laboratory by oxidizing ethyl alcohol, but it is actually obtained as a by-product in the distillation of wood. Vinegar is essentially a

dilute solution of acetic acid obtained by the oxidation of dilute alcohol by bacteria. Since it is a rather weak acid, it is used in the industries when a weak acid is desired.

SUMMARY OF CHAPTER XXIX

ORGANIC CHEMISTRY is the study of carbon compounds.

A STRUCTURAL FORMULA represents the arrangement of the atoms composing a molecule. Several compounds may have the same empirical formula. These are *isomers*.

A HYDROCARBON is composed of carbon and hydrogen only. The *methane series* has the general formula C_nH_{2n+2}; the *ethylene* series, C_nH_{2n}; the acetylene series, C_nH_{2n-2}.

PETROLEUM is a mixture of hydrocarbons. Gasoline, kerosene, and crude oil are obtained from petroleum by distillation. The yield of gasoline is increased by the decomposition of the higher boiling residues in the cracking process.

SUBSTITUTION PRODUCTS are those in which one or more hydrogen atoms of a hydrocarbon are replaced by some other element or radical, such as carbon tetrachloride.

ALCOHOLS may be thought of as being derived from hydrocarbons by the substitution of one or more hydroxyl groups for a corresponding number of hydrogen atoms. *Ethyl* alcohol is made by the fermentation of sugar. *Methyl* alcohol is a by-product of the distillation of wood and can be prepared from carbon monoxide. *Denatured alcohol* is ethyl alcohol to which some poison has been added.

ETHER is ethyl oxide. It is prepared by the action of sulfuric acid on alcohol.

ALDEHYDES contain the group $-\overset{H}{\underset{|}{C}}=O$. Formaldehyde, the commonest aldehyde, is made by oxidizing methyl alcohol.

ORGANIC ACIDS contain the carboxyl group $-\overset{OH}{\underset{|}{C}}=O$. They can be made by oxidizing aldehydes or alcohols.

Questions and Problems

1. Why are structural formulas so much used in organic chemistry?

2. What is the relation between carbon tetrachloride and methane?

3. What is the principal source of the paraffin series of hydrocarbons?

4. Why is it not economical to make grains into alcohol?

5. What group of elements is characteristic of organic acids?

6. What is the relation between ethyl alcohol and acetic acid?

7. Why is alcohol sometimes mixed with water to form a non-freezing mixture for the radiator of an automobile?

8. What is the catalyst used in fermentation?

9. Name five organic substances found in the home and describe how each was made.

10. How would you prove that carbon dioxide and water are formed when kerosene burns?

11. Sixty-nine grams of ethyl alcohol are burned. (*a*) What weight of carbon dioxide is formed? (*b*) of water?

12. How many liters of carbon dioxide result from the fermentation of 60 grams of glucose?

13. Under standard conditions a liter of methane weighs 0.72 grams. Compute (*a*) its molecular weight; (*b*) its specific gravity referred to hydrogen.

14. A certain carbon compound has the following composition: carbon 54.7%; hydrogen 9.1%; oxygen 36.2%. Its specific gravity (air = 1) is 1.53. Find its formula.

15. Another carbon compound has the same percentage composition as that in problem 14, but its specific gravity referred to air is 3.05. Find its formula.

Topics for Further Study

Industrial alcohol. How is industrial alcohol made? What laws govern its manufacture and sale? Why? In what way is the production of cheap alcohol of benefit to many industries? (Duncan's *Chemistry of Commerce* and Martin's *Modern Chemistry*.)

Solvents. Why does the industrial chemist and manufacturer need solvents other than water? What are such solvents? What new ones have recently been introduced and how have they changed the paint industry? What solvents do druggists use? paint manufacturers? perfumers? dry-cleansers? (*Chemistry in Industry*, vol. 1.)

CHAPTER XXX

FOOD AND CLOTHING

The carbohydrates: sugar, glucose, starch, cellulose — fabrics and paper — nitrocellulose.

Fats and oils — soap — edible oils — hydrogenation of oils.

Foods — kinds and uses — food values and composition — necessary quantity — vitamins.

373. Carbon compounds and living matter. It was originally thought that in some peculiar way organic compounds were different from inorganic compounds. Before the middle of the last century all organic compounds had been obtained directly or indirectly from living matter, and it was believed that a " vital force " was essential for their production. This view was shattered by the synthesis of several simple organic compounds from inorganic material. Since then a great many complicated organic substances of all classes have been synthesized from such purely inorganic matter as coal, calcium oxide, and water. We now know that there *is no essential difference between organic and inorganic compounds.*

In this chapter we shall consider a few of the rather complex substances which are the principal products of animal and plant life. These compounds are put to a number of uses and are essential foods for man and beast. We shall not be able to do more than outline the process of formation of these compounds in plants and animals, and shall only touch on their transformation during the life process. The branch of chemistry which deals with these matters is every day becoming more important, but is obviously too complicated to be considered here. It is called **biological chemistry.**

The Carbohydrates

374. Composition. Sugar, starch, cotton fiber, and wood fiber are all common substances of great importance. These materials and a great many others which are products of plant life belong to a class of carbon compounds called **carbohydrates.** The carbohydrates all contain carbon, hydrogen, and oxygen. The last two elements are always present in the same proportion as in water; hence one might imagine from the empirical formula that the substance were composed of carbon and a certain amount of water. This, of course, is not the structure of the compounds, but it has given rise to the name carbohydrates. We shall consider a few important carbohydrates.

Fig. 199. Sugar beet as grown in California.

Photograph from *Wide World Photos.*

Fig. 200. Maple-sugar season in Vermont.

375. Ordinary sugar ($C_{12}H_{22}O_{11}$). The substance commonly called **sugar** is obtained mainly from the sugar cane and the sugar beet (Fig. 199), although it also occurs in the sugar maple (Fig. 200) and in honey.

The juices of the sugar cane are extracted by crushing the stalks between rollers and evaporating the liquid thus obtained in vacuum pans. In this way the solution boils at a low temperature (about 65° C.), and the decomposition of a part of the sugar is prevented. When the sirup cools, the sugar crystallizes and the crystals are separated from the liquid by centrifugal machines. This gives brown sugar, which is usually refined by being dissolved in water and passed in solution through boneblack. The purified sirup is again concentrated in closed tanks, called vacuum pans (Fig. 201), and crystallized out. Sugar is extracted from the sugar beet in much the same way, and the product is identical with the cane sugar.

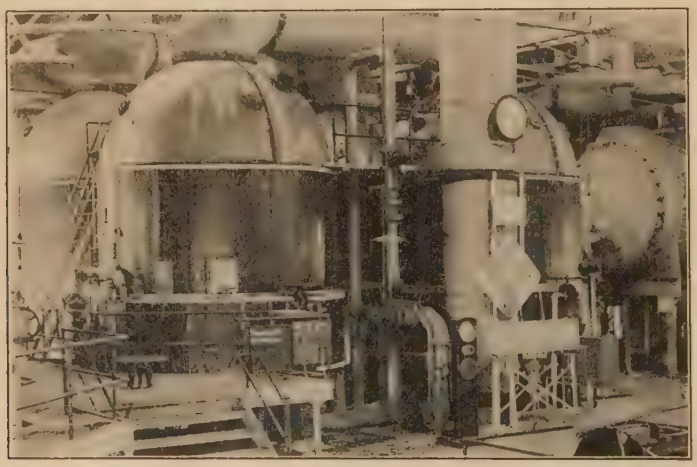


Fig. 201. Vacuum pans used to evaporate the sugar juice.

Since there are a great many different kinds of sugar, we speak of ordinary sugar as **cane sugar,** or **sucrose.** When cane sugar is boiled with water and a little acid to act as a catalyst, it forms two simpler isomeric sugars, **glucose** and **fructose;** this case of hydrolysis is often called **inversion:**

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Both of these sugars have a sweet taste, but not so sweet as cane sugar, and they crystallize with difficulty. Thus, a solution

of cane sugar when boiled with the addition of a little acid or similar substance is converted into a sticky mass which will not crystallize, a fact which is taken advantage of in making different kinds of candy.

376. Glucose, or grape sugar ($C_6H_{12}O_6$). This sugar occurs in many fruits and is often called grape sugar because of its presence in grape juice. It can be prepared from cane sugar or starch. The molecule of cane sugar is composed of a molecule of glucose and one of fructose joined together with the loss of water. So, too, a molecule of starch is probably made up of a great many molecules of glucose linked together. When starch is boiled with very dilute acid, it is broken down into glucose.

Let us boil a little starch with water into which have been put a few drops of hydrochloric acid to act as catalyst. Then we add enough sodium carbonate to neutralize the acid. The liquid is found to be sweet in taste because of glucose. We can test for glucose by adding Fehling's solution (§ 477), which gives a red precipitate of cuprous oxide (Cu_2O) on heating.

To understand the change of starch into glucose, we must note that starch has such a large molecule that we do not even try to write an exact empirical formula for it. It is sometimes written as $(C_6H_{10}O_5)_x$ since we do not know its molecular weight. This merely shows the relative number of atoms in the molecule without giving their total number. In this reaction the water decomposes the large molecules and combines with the material:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_x} + x\ H_2O \longrightarrow \underset{\text{glucose}}{x\ C_6H_{12}O_6}$$

We have here an example of hydrolysis.

This method is used commercially on a large scale for preparing glucose. The material is usually sold as a thick sirup under the name of **glucose,** or **corn sirup,** or as a mass of crystals. Glucose is used very extensively in the manufacture of jams, jellies, candies, and sirups. It is much cheaper than cane

sugar and although not quite so sweet can be used in place of the crystalline sugar for most purposes.

377. Starch ($(C_6H_{10}O_5)_x$). Starch is the most abundant of the carbohydrates. It is an example of those substances discussed in Chapter XVIII which form colloidal solutions. It is contained in large quantities in all grains and in potatoes. Starch is built up by plants from water and carbon dioxide under the influence of the energy from the sun. This is done in the plant through the agency of the green coloring material in the leaves, which is called **chlorophyll.** We do not know just how this remarkable synthesis takes place; it has been impossible to duplicate it in the laboratory. The sugars which occur in the sugar cane, the sugar maple, etc., are probably formed either by a similar synthesis, or else by the decomposition of some starch already formed by the plant.

Starch is usually obtained for commercial purposes from the potato or from corn. It is present in vegetable material as small granules, which are often incased in fibrous material. The cellular structure of the vegetable is broken up by grinding; the particles of starch are then washed away by a stream of water and collected. Starch is

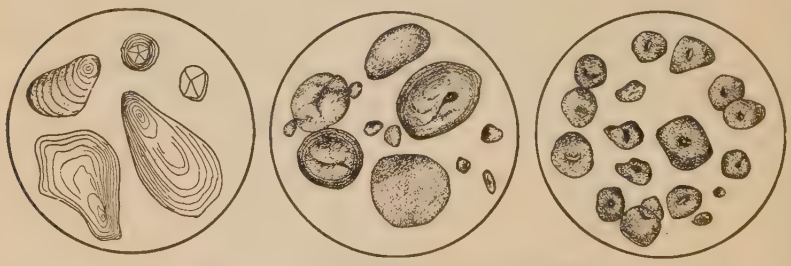


Fig. 202. Starch grains, greatly magnified.

insoluble in cold water but goes into solution in hot water, forming a *colloidal* solution. These colloidal solutions are used in the laundry for stiffening purposes.

The minute **granules of starch** differ somewhat in appearance (Fig. 202) according to the source of the starch. It is possible

with a microscope to determine from what plant any particular sample of starch was obtained. Since it is the main constituent of potatoes and all the grains, it enters very largely into the food of man. These starchy foods are made more digestible by cooking because in that process the starch granules burst. But before starch can be assimilated in the human body, it must be converted into the simpler sugars by the action of the digestive juices.

The **alcoholic fermentation** of starchy materials mentioned in the last chapter is one of the methods of preparing alcohol for industrial purposes. The starch is changed into sugar by the action of water in the presence of a catalyst (the enzyme diastase) which occurs in sprouting barley. It is usual to bring the grain or other source of starch into contact with some sprouted barley (malt). By the action of the enzyme the starch is thus converted into a sugar. Yeast is then added, and the alcoholic fermentation of the sugar takes place.

378. Cellulose ($(C_6H_{10}O_5)_n$). Cellulose is the principal material in the woody fiber of plants. Linen, cotton, hemp, and flax are chiefly cellulose. Absorbent cotton and the ordinary filter paper used in the laboratory are almost pure cellulose. This substance is another carbohydrate and has the same chemical composition as starch. We know nothing about the size of its molecules, but it is evidently more complicated than starch; so we write it as $(C_6H_{10}O_5)_n$. It is insoluble in water and most other solvents. When boiled with acids it is hydrolyzed into glucose.

379. Vegetable fabrics and paper. Vegetable fabrics like **cotton, linen,** and **jute** are composed of cellulose. The particular form in which this cellulose has been produced by the plant determines the nature of the thread and fabric. Paper is largely made from the cellulose obtained from wood, although the finer grades are manufactured out of linen and cotton rags.

Wood is composed of a rather impure form of cellulose; but in the manufacture of paper some of these impurities, which are colored resinous materials, are removed after the wood has been reduced to a

pulp. When this wood pulp is rolled out into thin sheets and dried (Fig. 203), we have a porous paper, such as filter paper, which is fairly pure cellulose. In order to make a paper that is suitable for writing and printing, the pulp is mixed with a number of inorganic solids, such as clay and chalk; these substances are called fillers and lend rigidity and body to the paper. Most papers are given a smooth coating by treating them with some substance like casein (from milk), which can be ironed into the hard surface necessary for writing and printing.

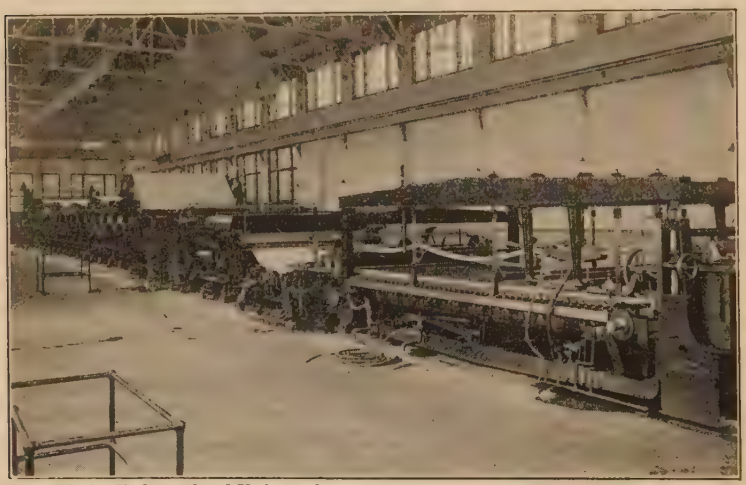


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Fig. 203. Paper-making machine.

Cheap paper is made from so-called "mechanical pulp." This is wood which has merely been ground to a pulp by a sort of grindstone. Such paper contains most of the original impurities of the wood and soon turns yellow and becomes brittle. Better grades of paper are made from pulp which has been purified by treatment with sodium hydroxide, bleaching powder, or sodium sulfite. These chemicals remove the impurities from the cellulose.

Paper made from mechanical pulp gives a yellow color when treated with a water solution of aniline ($C_6H_5NH_2$). Newspapers and wrapping papers will give this test; writing paper usually will not.

380. Silk and wool. The animal fabrics, **silk** and **wool**, are not carbohydrates. They are complex nitrogen compounds. The essential difference, however, between the appearance of silk and cotton is due to the mechanical structure of the fiber and not to its chemical constitution. Figure 204 shows the difference between these fiber structures. A thread of silk

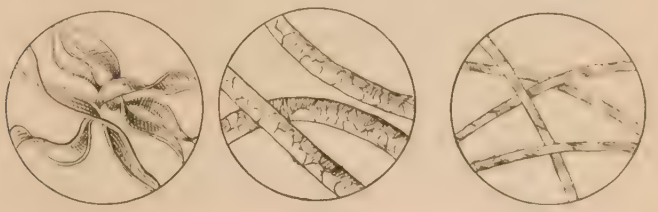

Fig. 204. Three textile fibers, greatly magnified.

is one continuous, long tube, which causes the well-known appearance of silk material.

Cellulose can be converted into a long fiber which somewhat resembles that of silk. This is done by dissolving it in certain solvents and then squirting the solution through a very fine hole into a second solution, which immediately causes the cellulose to be reprecipitated in the form of a fine, long, continuous thread. When these threads are woven into a fabric, the product closely resembles pure silk and is called **rayon**, or artificial silk. The material is, however, still cellulose.

Mercerized cotton is made by treating cotton cloth under tension with sodium hydroxide. After washing and drying, the cloth has a somewhat silky appearance and is stronger than ordinary cotton cloth.

381. Nitrocellulose. When cellulose is treated with a mixture of sulfuric and nitric acids, it forms an ester of cellulose and nitric acid. This action probably takes place because of a certain number of hydroxyl groups which are present in the cellulose molecule. According to the concentration of the acid and

the way in which the reaction is carried out, a varying amount of nitric acid can be made to react with the cellulose. The products are called **nitrocellulose.**

Nitrocellulose, which contains relatively little nitrogen (called the **lower nitrates**), is used in the preparation of smokeless powder. **Collodion** is a solution of the lower nitrates in a mixture of alcohol and ether. When these solvents evaporate, they leave a thin film of material, which is used for coating photographic plates and for similar purposes. Collodion is often sold under the trade name of "**new-skin**" or "**liquid court-plaster.**" Lacquers (§ 499), used for painting automobiles, are solutions of nitrocellulose in organic solvents. **Celluloid** is made by heating a mixture of camphor and nitrocellulose. It is consequently very inflammable and ignites with almost explosive violence. The **higher nitrates** are called **guncotton** and are used as the explosive in torpedoes.

Fats and Oils

382. Fats and oils are esters. Both plants and animals form a number of substances which are classed as **fats** and **oils.** The plant products are usually liquids and are called **oils;** for example, olive oil and cottonseed oil. Similar substances are made in the animal body from the vegetable oils which it consumes. These are semi-solids and are called **fats,** such as butter and lard. All these substances may be broken down by heating with water and a catalyst to yield a mixture of organic acids of high molecular weight and an alcohol with 3 OH-groups — **glycerol** ($C_3H_5(OH)_3$). A compound which can be hydrolyzed in this way is called an **ester.** The two most important acids which occur in fats are palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$).

An example of a very simple ester is ethyl acetate, which can be made from ethyl alcohol and acetic acid:

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction is slowly reversible, and by changing the conditions we can prepare the ester or decompose it by hydrolysis. The

simple esters of low molecular weight are low-boiling liquids of pleasant odor and are used in the preparation of lacquers (§ 499).

383. Soap. The most convenient method of decomposing an ester is to heat it with sodium hydroxide:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{alcohol}}{C_2H_5OH}$$

If we apply this procedure to animal fats, we obtain the sodium salts of acids of high molecular weight. This mixture of salts is soap, and the general reaction is called **saponification.** The glycerol obtained as a by-product is a viscous liquid used in the manufacture of dynamite. The following equation represents such a reaction:

$$\underset{\text{glyceryl stearate}}{\overset{\text{Fat}}{(C_{17}H_{35}COO)_3C_3H_5}} + \overset{\text{Alkali}}{3\,NaOH} \longrightarrow \overset{\text{Soap}}{3\,\underset{\text{sodium stearate}}{C_{17}H_{35}COONa}} + \overset{\text{Glycerol}}{C_3H_5(OH)_3}$$

Fig. 205. Soap kettle which contains enough stock to make 10 or 12 carloads of soap.

It is not expected that the above equation will be memorized, but it is given in order to show that the reaction for making soap is similar to that for making sodium acetate. The sodium

salts are only moderately soluble in water and can be separated from the reaction mixture by the addition of common salt. In making soft soap, potassium hydroxide is used instead of sodium hydroxide.

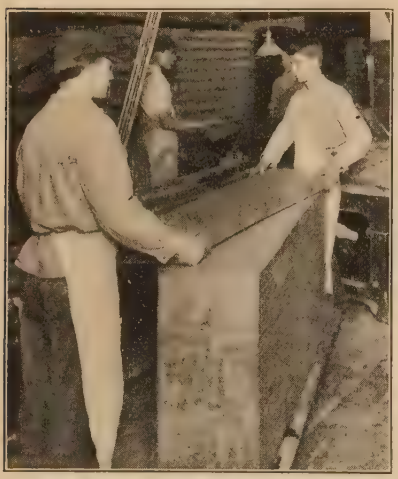

Fig. 206. Cutting soap into bars and then into cakes.

In the commercial manufacture of soap the fat and the alkali are heated together in huge kettles (Fig. 205) for several days. The soap is *salted out* and rises to the top of the liquid. The glycerol, which is the other product of the reaction, is separated by distillation from the liquid containing the *spent lye*. A great variety of soaps can be manufactured, according to the nature of the fat which is used and the way in which the process is carried out (Fig. 206).

384. Cleansing power of soap. The following seems to be the explanation of the cleansing power of soap and soap solutions. Soap is a mixture of the sodium salts of very weak acids. Consequently, when it is dissolved in water, the salts are almost completely hydrolyzed into free fatty acids and sodium hydroxide. These free fatty acids do not, however, precipitate out but stay in colloidal solution, probably because they combine with some of the undissociated soap. A solution of soap is therefore essentially an alkaline colloidal solution, and its cleansing action is connected with this fact. It is a more or less general property of colloidal solutions that the colloid tends to bring other substances into colloidal solution and to prevent the precipitation of substances from colloidal solution. This is an example of the *mutual protection of colloids*. When oil is shaken with soap solution, the oil remains in the solution

permanently suspended in what is essentially a colloidal solution. In the same way particles of dirt are brought into colloidal solution by soapy water.

385. Edible oils. Fats and oils are used extensively as foods. For a great many culinary purposes it is necessary to have a solid fat; hence the animal fats are used in cooking to the almost complete exclusion of the vegetable oils. The only difference between these compounds is a few hydrogen atoms more or less, since the oils are esters of an acid with fewer hydrogen atoms than stearic acid. Recently a process has been devised by which these hydrogen atoms can be added artificially. The vegetable oil is heated and mixed with a certain catalyst, usually finely divided nickel. Hydrogen gas is then blown through the mixture and under the influence of the catalyst is absorbed by the unsaturated oil, thus producing the ester of a fatty acid with a much higher melting point. The nickel is filtered off while the mixture is still hot. On cooling, the mass sets to a solid which in every way resembles an animal fat. This process is called the **hydrogenation of oils.** The product is used as a substitute for animal fats in cooking (Crisco) and in the manufacture of soap.

Foods

386. Uses of different kinds of foods. The food we eat serves *three distinct purposes:*

(1) To build up new parts and replace worn-out ones;

(2) To keep the body at the required temperature;

(3) To supply the energy which enables us to work.

It is convenient to divide our foods into four classes according to their composition and the purposes they serve. The **carbohydrates,** such as starch and sugar, furnish both heat and body energy and also assist in building fats in the body. The **fats** — for example, butter, meat fat, and olive oil — produce both heat and energy. To some extent they form layers of protective tissue which may serve as a reserve food supply.

The **proteins,** which are chemically very complex substances, are *foods rich in nitrogen;* for instance, lean meat and the white of eggs. These replace the worn-out muscle tissue. The proteins have been carefully studied by the German chemist Fischer (Fig. 207). Finally, various **mineral compounds** are needed in the body to serve a great variety of uses. The quantities of iron, chlorine, sulfur, phosphorus, calcium, magnesium, sodium, and potassium which are required are extremely small. These substances are usually supplied in common salt, meat, fruit, and vegetables.

Fig. 207. Emil Fischer (1852–1919). Brilliant organic chemist who studied the carbohydrates and proteins.

387. Value of food. Many articles of food contain compounds which represent all four classes of food substances, but the proportion of carbohydrates, fats, and proteins in them varies greatly (Fig. 208). Milk probably contains all of these food substances in about the proportion in which they are needed in the body. The composition of cow's milk averages approximately as follows:

Water	87.2%
Casein (nitrogenous matter)	3.6%
Butter fat	3.6%
Lactose (milk sugar)	4.9%
Mineral matter	0.7%

It is the casein which is used in the manufacture of *cheese.* When milk sours, the lactose changes by fermentation to *lactic acid.* This change is brought about by certain bacteria.

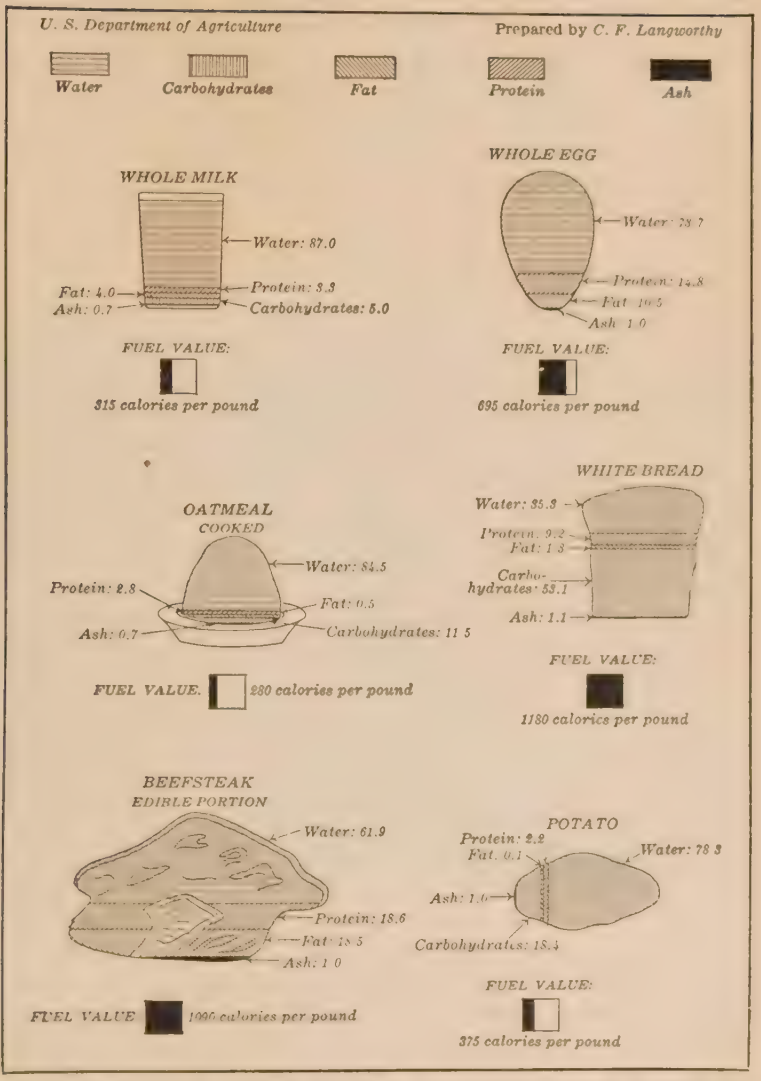

Fig. 208. Diagram to show the proportion of carbohydrates, fats, proteins, and water in some common articles of food.

Since foods act partly as fuels to supply the necessary heat and energy, we may determine their heat value very much as we determine the heat value of coal. The following table, taken from Sherman's "Chemistry of Food and Nutrition", shows the percentage composition and fuel value in Calories * per pound of the edible portion of a few common foods.

	Water	Carbo-hydrate	Fat	Protein	Ash	Fuel Value
Apples	84.6	14.2	0.5	0.4	0.3	285
Bacon	20.2		64.8	9.9	5.1	2840
Bananas	75.3	22.0	0.6	1.3	0.8	447
Beans, dried	12.6	59.6	2.9	22.5	3.5	1565
Beef, round steak	73.8		7.9	22.1	1.2	694
Bread, white	35.3	53.1	1.3	9.2	1.1	1199
Butter	11.		85.0	1.0	3.0	3491
Corn, green	75.4	19.7	1.1	3.1	0.7	455
Eggs	73.7		10.5	14.8	1.0	672
Oatmeal	7.3	67.5	7.2	16.1	1.9	1811
Potatoes	78.3	18.4	0.1	2.2	1.0	374
Tomatoes	94.3	3.9	0.4	0.9	0.5	104

388. How much food do we need? In recent years an immense amount of experimental study has been devoted to this subject, and the authorities do not altogether agree in their results. In general, however, it is considered that the total energy value of an adult diet should be not less than 3000 Calories a day. It is evident, of course, that this value will depend somewhat on the nature of the work which one is doing. Then, too, there are many other factors which affect the process of digestion but which are difficult to measure, such as the appetizing character of the food and the nervous condition of the person.

The amount of protein required for building up and replacing the worn-out parts of the body is probably a great deal less than that consumed in our usual diet; the balance of the

* The Calorie used here is the large Calorie, which is the amount of heat required to raise the temperature of 1 *kilogram* of water 1° C

protein food which we eat is merely consumed as fuel. It must not be thought that the proteins alone supply the material for replacement and growth. Both fats and carbohydrates are also concerned in this process although their chief use is to supply energy. It would seem as if 75 grams (about 3 ounces) of protein per day were sufficient for the average adult; this is much less than most of us eat.

389. Vitamins. In addition to the foods that we have considered, the animal system must also have an adequate supply

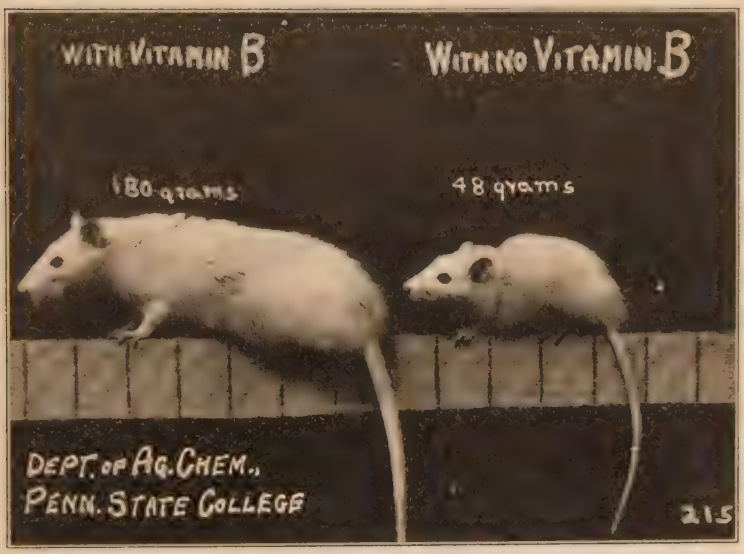

Fig. 209. These rats are of the same age and have received the same rations with the exception of Vitamin B.

of water and inorganic salts, which are obtained without difficulty in the food. Recently a great deal of interesting evidence has been accumulated showing that very minute amounts of certain compounds also seem to be essential to the growth and healthy condition of animals (Fig. 209). These substances are

called **vitamins**; they have not yet been definitely identified or isolated. They appear to be substances analogous to catalysts. Certain diseases, such as *beri-beri* and *scurvy*, have been shown to be due to their absence in the diet. In general, it can be said that a widely distributed diet will insure a sufficient supply of these accessory factors.

Because of the extreme complexity of the reactions which go on in the body, the whole problem of nutrition is a very difficult one. The heat values of foods, such as those shown in the table, are of some help in determining the proper diet; but obviously one must be very careful in drawing any conclusions from such inadequate data. These energy values do not take into account the protein requirement, the digestibility of the food stuff, or the need and importance of accessory factors.

SUMMARY OF CHAPTER XXX

NO ESSENTIAL DIFFERENCE exists between organic and inorganic compounds. Many organic compounds may be prepared in the laboratory from inorganic material.

CARBOHYDRATES are compounds which contain carbon combined with hydrogen and oxygen in the proportion in which they occur in water. Sugar, starch, and cellulose are important carbohydrates.

ORDINARY SUGAR is made from sugar cane or sugar beet. On being boiled with water in the presence of an acid, it is hydrolyzed into *glucose* and *fructose*.

STARCH is obtained commercially from corn or potatoes. Starch may be broken down into glucose by dilute acids, or by an enzyme in sprouting barley. This change is brought about before the alcoholic fermentation of grains and starch.

CELLULOSE is a carbohydrate which constitutes the fibrous material of plants. Cotton, linen, and paper are mainly cellulose, but wool and silk are not.

NITROCELLULOSE is made by the action of nitric acid on cellulose. It is the basis for smokeless powder, collodion, lacquers, and celluloid.

FATS AND OILS are the glycerol esters of organic acids. Vegetable oils differ from animal fats by only a few hydrogen atoms, which can be added artificially by means of a catalyst.

SOAPS are sodium salts of the higher fatty acids. They are formed by the action of sodium hydroxide on fats.

FOODS serve (1) as fuel to supply energy for doing work, (2) as fuel to keep the body warm, and (3) to furnish material to repair worn-out and growing parts.

FOUR CLASSES OF FOODS are *fats, carbohydrates, proteins,* and *mineral compounds.* Fats and carbohydrates furnish primarily the necessary energy. Proteins (nitrogen compounds) are essential to growing organisms and are necessary for replacing wear and tear.

THE AVERAGE ADULT needs food which will furnish about 3000 Calories per day and which contains about 75 grams of protein, besides small but indispensable amounts of mineral compounds.

CERTAIN MINUTE AMOUNTS of substances have been found to be essential in the diet. These substances are called *vitamins.*

Questions and Problems

1. How does a hydrocarbon differ in composition from a carbohydrate?
2. Why are vacuum pans used in concentrating sugar solutions?
3. How could you prove that a piece of filter paper contained carbon?
4. How would you test for the presence of grape sugar?
5. Describe the steps in the process of making alcohol from potatoes.
6. In preparing starch from corn, why is cold water used instead of hot?
7. What is the difference between sucrose and glucose? between collodion and celluloid?

8. What valuable by-product is obtained in the manufacture of soap?

9. What is the distinction between a fat and an oil?

10. What is the difference between oils made from petroleum and vegetable oils?

11. What is the danger in putting formalin into milk as a preservative?

12. Why should oatmeal be thoroughly cooked?

13. What difference should be made between summer and winter diets?

14. What difference should be made between the diet of a bank clerk and that of a blacksmith?

15. Name three articles of food which are rich in carbohydrates, in fats, in proteins.

16. Why is an abundant supply of pure water necessary for the digestion and assimilation of our food?

17. How many pounds of glycerol can be obtained from 198 pounds of fat (glyceryl stearate)?

18. How many grams of pure carbon can be obtained from 85.5 grams of dry sucrose?

19. A certain carbohydrate contained 42.1% carbon, and the rest was oxygen and hydrogen. What is the simplest formula?

20. How much will it cost for the caustic soda needed to make 1 ton (2000 lbs.) of soap (sodium stearate)? Assume that the caustic soda is 76% pure and costs $3.10 per 100 lbs.

Topics for Further Study

Sugar. Has sugar always been an essential part of man's food? How is sugar obtained from the sugar cane and sugar beet? What is molasses? What familiar articles of food contain large amounts of glucose? How is it made, and is it a desirable food? Is saccharin a sugar? (Slosson's *Creative Chemistry*, *Chemistry in Agriculture*, and Martin's *Modern Wonders*.)

Essential materials from wood and cotton. What is the chief constituent of wood fiber and cotton? What are some of the important things into which it can be converted? What is the chemical relationship between rayon, smokeless powder, "new-skin," writing paper, a photographic film? How is each made? (Slosson's *Creative Chemistry* and *Chemistry in Industry*, vols. 1 and 2.)

Foods. What important changes in our ideas concerning the value of foods have taken place since 1910? On what experimental evidence is this based? How are foods tested for vitamin content? How are fuel values of foods determined? (*Chemistry in Agriculture* and Howe's *Chemistry in the World's Work.*)

Review Questions

1. How many volumes of oxygen are required to burn one volume of methane to carbon dioxide and water?

2. Give the formula and state one use of each of the following: (*a*) *sal ammoniac*, (*b*) *graphite*, (*c*) *cooking soda*, (*d*) *vinegar*, (*e*) *laughing gas.*

3. What elements occur commonly in organic substances? How can their presence be shown?

4. What is soap? How is it made? What is the difference between hard and soft soap?

5. Name three general classes of foods and show in which class or classes each of the following should be placed: (*a*) *butter*, (*b*) *lean meat*, (*c*) *milk*, (*d*) *wheat bread*, (*e*) *egg.*

CHAPTER XXXI

MAGNESIUM AND CALCIUM

Magnesium, its preparation and properties — magnesium oxide and hydroxide — magnesium salts.

Calcium, its preparation and properties — calcium carbonate — hard water — methods of softening water — lime — calcium hydroxide — mortar — cement — other calcium compounds.

Strontium and barium.

390. General characteristics. We shall now study two metallic elements, magnesium and calcium, which belong to Group II in the periodic table. Next to aluminum and iron they are the most abundant of the metallic elements (Fig. 13) although they never occur in the free state. Many common mineral substances, such as soapstone, asbestos, marble, and limestone, are compounds of these elements. From the very abundant supply of limestone, many important building materials, such as plaster and cement, are prepared by chemical processes. There are also two other members, strontium and barium. This family is sometimes called the **alkaline earths.** The metal radium also belongs here, but it is such an unusual element that we shall devote a whole chapter to its description. These elements are all very active metals which form positive divalent ions; they show no nonmetallic properties.

Magnesium

391. Compounds found in nature. Magnesium occurs as **magnesite** ($MgCO_3$) and as a double carbonate **dolomite** ($MgCO_3 \cdot CaCO_3$). There are also several natural silicates of

magnesium which are familiar and useful substances. These are **meerschaum, talc** or **soapstone,** and **asbestos.** Soapstone is used for sinks and table tops and when powdered is known as talcum powder or French chalk. Asbestos is a fibrous mineral, which is manufactured into fireproof cloth and cardboard. In

Fig. 210. Sawing marble in a Vermont quarry.

the Stassfurt deposits magnesium occurs as a sulfate and as a double chloride with potassium.

392. Preparation and properties of the metal. Metallic magnesium is made by the electrolysis of fused salts, in the same way that such metals as sodium and aluminum are prepared. A mixture of magnesium, potassium, and sodium chlorides is used. A carbon rod forms the anode and an iron crucible the cathode. The molten metal collects on the sides and bottom of the crucible. When cold the mass is broken up and the metal removed. It is usually put on the market in the form of a fine powder or as a thin ribbon.

Magnesium is attacked by moist air and forms a white crust consisting of basic magnesium carbonate. It burns in air with a brilliant white light, producing the oxide (MgO) and the nitride (Mg_3N_2); **flash-light powder** consists of a mixture of magnesium powder and potassium chlorate. Certain kinds of **signal lights** and **fireworks** contain powdered magnesium. The metal reacts slowly with boiling water to form hydrogen:

$$Mg + 2\,H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$$

It displaces hydrogen rapidly from cold dilute acids.

393. Magnesium oxide and hydroxide. The oxide (MgO) is made by heating magnesium carbonate; it is called **magnesia.** It is a very infusible substance and is used for making fireproof bricks and the linings for high-temperature furnaces. It combines slowly with water, forming a hydroxide ($Mg(OH)_2$). This hydroxide is an insoluble white substance which finds some uses in medicine under the name of **milk of magnesia.** It is formed when a soluble base is added to a magnesium salt:

$$MgSO_4 + 2\,NaOH \longrightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

394. Magnesium salts. Magnesium carbonate ($MgCO_3$) occurs naturally and is the source of magnesium oxide and hydroxide. It is insoluble in pure water, but soluble in water containing carbon dioxide. A *magnesium bicarbonate* is formed:

$$MgCO_3 + H_2CO_3 \longrightarrow Mg(HCO_3)_2$$

Magnesium sulfate ($MgSO_4$) is a constituent of some natural waters and occurs in certain salt deposits. It is often called **Epsom salts** and is used in medicine because of its laxative properties. **Magnesium chloride** is found in sea water. In hot water this salt forms hydrochloric acid by hydrolysis:

$$MgCl_2 + H_2O \longrightarrow MgO + 2\,HCl$$

The acid corrodes metals, and hence sea water cannot be used in ships' boilers.

Calcium

395. Preparation and properties of the metal. Metallic calcium also is made by the electrolysis of a fused salt. Calcium chloride is used for this purpose.

The salt is fused in a graphite crucible, which forms the anode, and an iron rod is used as the cathode. The metal which is liberated around the rod adheres to it, and as this rod is gradually raised a stick of metallic calcium is pulled from the melt. It is a silver-white metal about as hard as lead and cannot easily be cut with a knife. It has a brilliant luster, which is soon dulled by moist air. Water is slowly decomposed by calcium, and hydrogen is evolved:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

When heated to a temperature above its melting point, it burns brilliantly, forming the oxide (CaO). Metallic calcium has few commercial uses.

396. Calcium carbonate ($CaCO_3$). This compound is the commonest form in which calcium is found. The purest variety is **Iceland spar,** which is crystalline and as transparent as glass. **Marble** is almost pure calcium carbonate. It is composed of a mass of tiny crystals cemented together and is often as white as snow. **Limestone** is the most abundant form of calcium carbonate, but shows less of the crystalline structure than marble, and is often of a cloudy gray color. We believe that limestone was formed in some previous geological age from the shells of sea animals.

Calcium carbonate is insoluble in water but like the magnesium compound is soluble in water containing carbonic acid, producing calcium bicarbonate:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

Calcium carbonate reacts with acids, giving carbon dioxide:

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

Pure calcium carbonate can be made in the laboratory by adding some soluble carbonate to a soluble calcium salt:

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 \downarrow + 2\,NaCl$$

Prepared in this way it is a white powder called **precipitated chalk** (not crayon) and is used in polishing powders (tooth paste); as **whiting** it is mixed with linseed oil to make **putty.** The natural forms of calcium carbonate are put to many uses besides that of preparing lime and carbon dioxide; for example, it is used as a flux in blast furnaces, in making soda and glass, as well as for a building stone and as ballast for roads.

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Fig. 211. Limestone caves — stalactites and stalagmites.

397. What makes water hard? All natural water except rain water contains a certain amount of dissolved salts. Water in which there is a considerable amount of certain dissolved material is called **hard water.**

Magnesium and calcium bicarbonates are among the chief ingredients of the hard water which is found in some localities. These materials can very easily be dropped out of solution by simple boiling; carbon dioxide is expelled, and the insoluble carbonate is precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

The hardness due to these salts is called **temporary hardness.** Salts such as magnesium sulfate and calcium sulfate cannot

be removed by simple boiling, and water containing them is said to be **permanently hard.** In certain limestone regions all the water contains a great deal of temporary hardness. If it drips from some high place, as for instance from the top of a cave, it loses some of its carbon dioxide and slowly precipitates calcium carbonate. This material often accumulates in the form of long strips like icicles. The **stalactites** and **stalagmites** found in certain limestone caves are formed by this process (Fig. 211).

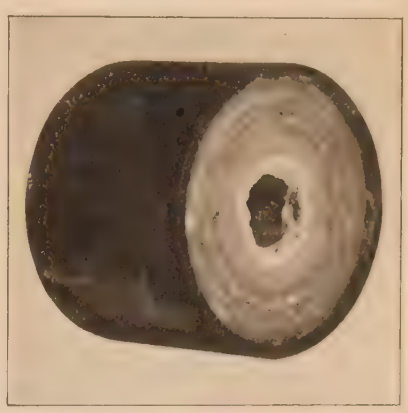


Fig. 212. Boiler scale in a tube.

398. Results of using hard water. Hard water is very undesirable for industrial and household use for two reasons. In the first place, when such water is used in a boiler, it deposits on the inside a heavy crust called **boiler scale.** This crust is a very poor conductor of heat and greatly cuts down the efficiency of the boiler (Fig. 212). In the second place, hard water is unsuitable for washing purposes because it will not easily form a lather with soap. Soap reacts with salts of calcium and magnesium, producing insoluble calcium and magnesium salts of the fatty acids:

$$2\,C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

These salts (often called **calcium** or **magnesium soaps**) are insoluble and form sticky particles in the water. Considerable soap must be used up in this way before the colloidal solution of soap is produced and a lather can be formed. This is, of course, very wasteful.

399. Softening water in the household. Hardness may be removed from water by a number of different methods; the process is called **softening water.** *Temporary hardness may be removed by* ***boiling*** *the water* for a short time; the insoluble carbonates are thus precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Temporary hardness can also be removed by the action of ***lime;*** this is done by stirring the water with the exact amount of lime necessary to cause the following reaction to take place:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$

The precipitate is then filtered from the softened water.

Permanent hardness cannot be removed by these methods. Sodium carbonate will remove permanent hardness by precipitating calcium or magnesium carbonates:

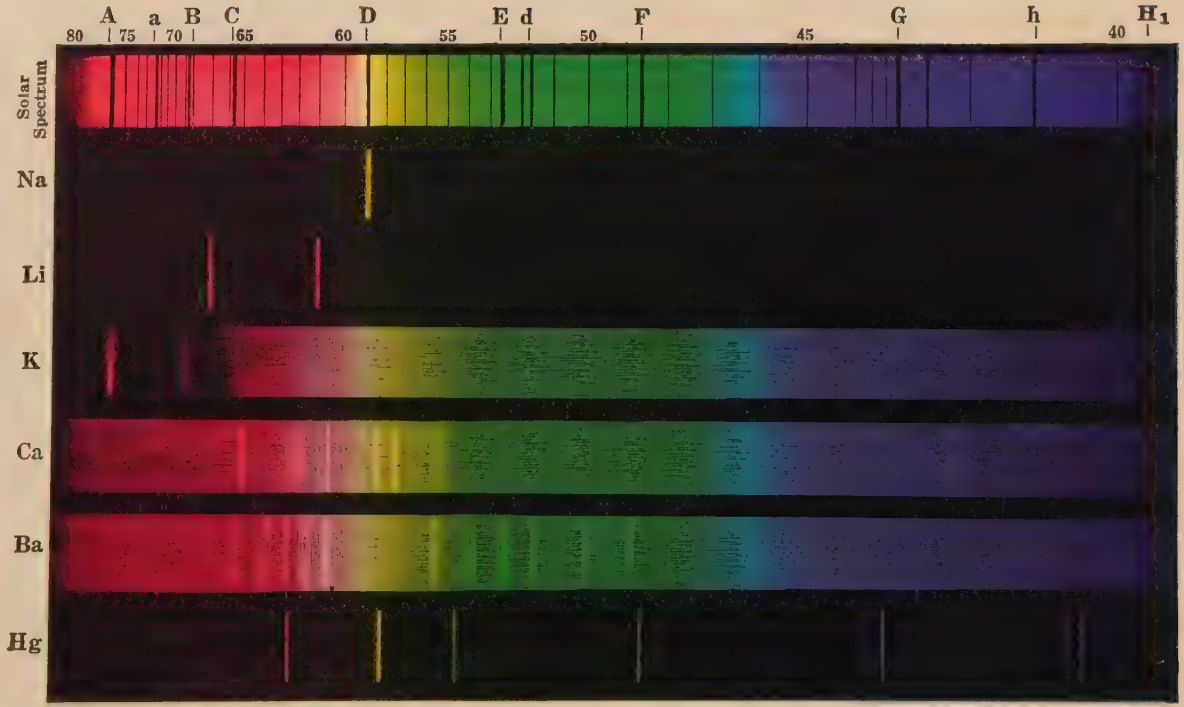
$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

Industrially the softening of water is carried out on a large scale, and the precipitated material is filtered off from the water, which is then ready for use. In the household the softening is often brought about on a small scale by the use of certain preparations, which are widely sold. Sodium carbonate under the name of **washing soda** is often employed. A small amount of it is added directly to the water before the soap is introduced. It removes all temporary and permanent hardness, as just explained. An excess of sodium salts has no deleterious effect on the soap. Ammonium hydroxide under the name of **household ammonia** is often employed in washing. It precipitates calcium carbonate from temporary hard water and from water containing both permanent and temporary hardness. Ammonium carbonate, formed from the calcium bicarbonates, acts like washing soda in removing permanent hardness:

$$Ca(HCO_3)_2 + 2\,NH_4OH \longrightarrow CaCO_3\downarrow + (NH_4)_2CO_3 + 2\,H_2O$$

$$CaSO_4 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + (NH_4)_2SO_4$$

Magnesium salts cannot be precipitated in this way. Borax ($Na_2B_4O_7$) is a salt of a very weak acid, and therefore its solution contains sodium hydroxide, which acts like ammonium hydroxide in softening the water.



SPECTRUM CHART.

400. Softening water for industries. A new method of softening water, called the **permutite process**, consists in filtering the water through an artificial sodium silicoaluminate. The calcium and magnesium in the water are exchanged for sodium in the permutite, a coarse sand-like material (Fig. 213). After 12-hours' use one tank is filled with brine and allowed to stand the same length of time, while the sodium in the brine replaces the calcium in the filter. Then the calcium chloride solution is drained off, and the filter is again ready for use. Thus we see that only salt is consumed, and the original charges last for years.

For convenience, the permutite radical may be indicated by Pe and the process of softening water as follows:

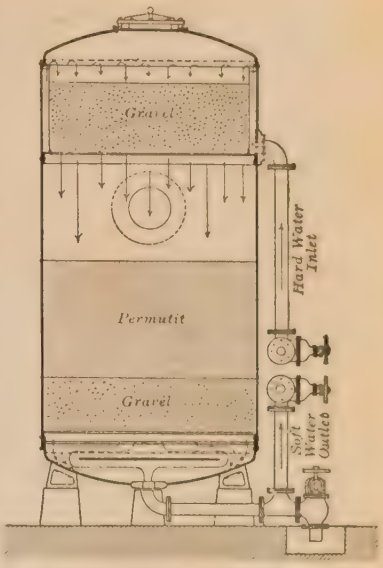


Fig. 213. Diagram of a permutite tank.

$$Na_2Pe + CaSO_4 \longrightarrow CaPe + Na_2SO_4$$

The reaction for the regeneration of the filter by brine is as follows:

$$CaPe + 2\,NaCl \longrightarrow Na_2Pe + CaCl_2$$

401. Lime, or calcium oxide (**CaO**). When limestone ($CaCO_3$) is heated, it gives off carbon dioxide, and calcium oxide is left as a solid:

$$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$$

This reaction is reversible, and unless the gas is continually removed, the action works backward. The process is carried out on a large scale in a furnace called a **kiln** (Fig. 214).

The hot gases from a suitable fire pass through the coarsely ground limestone, which is thus heated to the desired temperature. The calcium carbonate decomposes according to the reaction previously given,

and the carbon dioxide is removed by a strong draft through the kiln. In this way the action goes to completion at about 700° to 800° C. The product is often called **quicklime.**

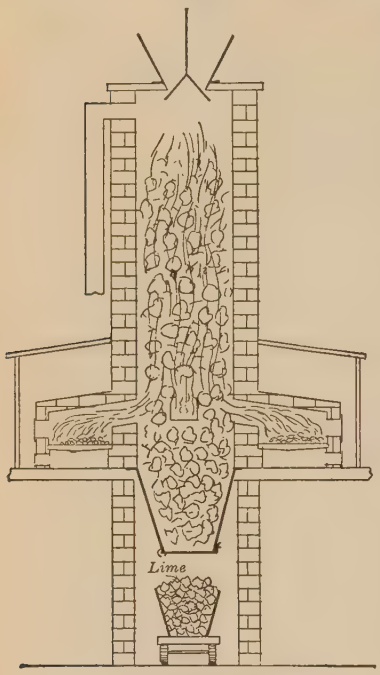


Fig. 214. Modern limekiln.

402. Quicklime, its properties and uses. Quicklime (CaO) is a white amorphous substance. It can be melted only with the greatest difficulty. When heated strongly, it glows with a brilliant light and hence was formerly employed in **limelights.** Calcium oxide combines with water very rapidly and vigorously to form calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The reaction takes place with the evolution of much heat; it is called **slaking.** When exposed to air, quicklime slowly absorbs carbon dioxide and moisture. It is then said to be air-slaked and cannot be used for most purposes.

403. Slacked lime, or calcium hydroxide ($Ca(OH)_2$). The chief use of quicklime is in the preparation of **calcium hydroxide,** or, as it is often called, **slaked lime.** The hydroxide is a white substance, only slightly soluble in water. A clear solution is called **limewater.** A suspension of the hydroxide in water is called **milk of lime** and is generally employed when we wish to use calcium hydroxide.

Calcium hydroxide is a fairly strong base although we cannot obtain concentrated solutions of it because of its insolubility.

It is a very cheap substance and is therefore selected whenever an alkali is desired of which a concentrated solution is unnecessary. It is used to remove the hair from hides. Finely ground limestone and air-slaked lime are added to soils to neutralize their acidity. Lime is also employed very extensively as **whitewash** and in the preparation of **plaster** and **mortar**. It is usually prepared as needed by the slaking of quicklime; it is the latter substance which is generally sold under the name of lime.

404. Mortar and plaster. **Mortar** is a *mixture of slaked lime and sand*. It is used for holding together bricks and stone in the construction of buildings, walls, etc. It is exposed to the air for a long period in contact with a porous surface and under these conditions sets to a hard mass, which effectively binds the materials together. The setting of mortar is due largely to the going into solution of a more soluble form of the hydroxide and the slow crystallization of a stable hydrated form in interlacing crystals. The absorption of carbon dioxide from the air takes place very gradually and eventually converts some of the material to carbonate. The crystals of hydrated calcium hydroxide interlace with the sand and form a rigid though porous structure.

Plaster is also made from freshly slaked lime and sand, but it generally contains hair in addition. This material serves to hold it together. The setting of plaster is exactly like that of mortar. Recently a mixture of lime and cement has come into use, which makes the use of hair unnecessary. An outer coating consisting of lime and plaster of Paris together with a little glue is put on when the plaster is nearly dry.

Plaster of Paris is made by heating gypsum ($CaSO_4 \cdot 2\ H_2O$) until about three-fourths of the water of crystallization is driven off:

$$\underset{\text{gypsum}}{2\ CaSO_4 \cdot 2\ H_2O} \longrightarrow \underset{\text{plaster of Paris}}{(CaSO_4)_2 \cdot H_2O} + 3\ H_2O$$

Let us mix enough plaster of Paris with water to make a stiff paste. We may then put a medal on a glass square, oil them both, and pour the paste over the medal, allowing it to dry for half an hour; the plaster cast is then removed.

Plaster of Paris takes up water of crystallization and forms a hard mass. It is therefore useful for making copies of statuary and for surgical bandages.

405. Cement. Mortar, which is composed of the somewhat soluble calcium hydroxide, cannot be used under water. A material called **cement** will set to a hard, rocklike mass even under water; it can therefore be employed in the construction of dams, foundations for bridges, and similar objects. It is also superior to mortar and plaster in strength and firmness.

Cement is made by heating a mixture of limestone and clay, or of natural rocks which have these constituents in the proper proportion. The mixture is pulverized to a fine powder and slowly fed into an inclined revolving cylinder, through which hot gases from a fire are passed (Fig. 215). In this way the material is subjected uniformly to the required temperature and finally falls out of the end of the revolving cylinder. The "clinker," as it is called, is cooled and ground to a very fine powder. In the process of heating, a

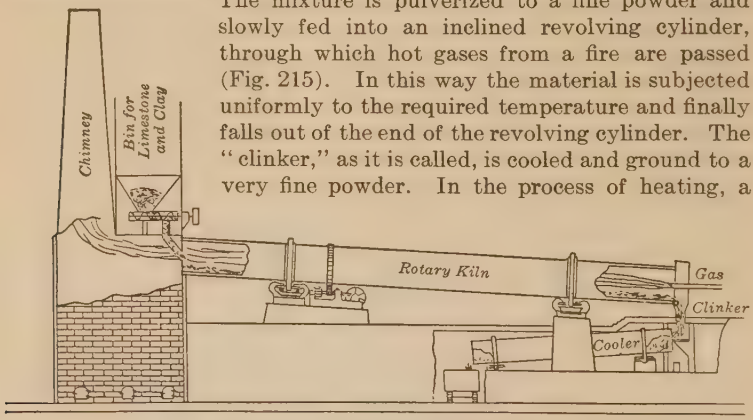
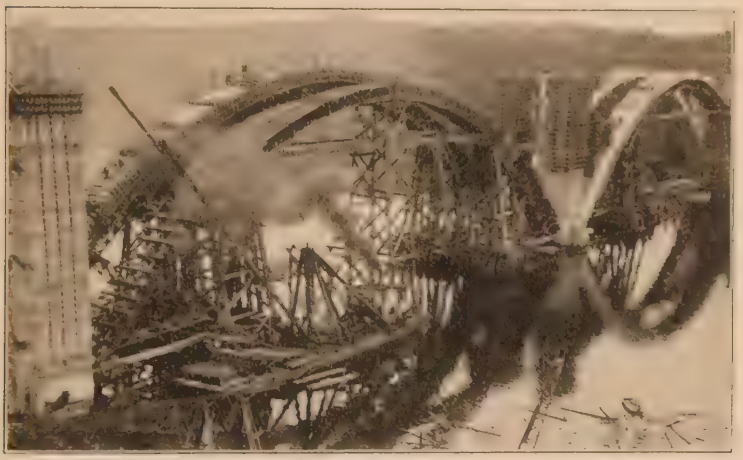


Fig. 215. Rotary cement furnace.

certain amount of water and carbon dioxide is driven off from the mixture. When this dehydrated powder is made into a paste with water, it slowly unites with some of the water and forms a material as hard as rock. It resembles a stone found in Portland, England, whence the name **Portland cement.**

The chemistry of the setting of cement is not well understood. It involves the *hydration of the silicates* in the mixture and probably also of calcium oxide. The crystals of the hydrated silicates and of calcium hydroxide interlace and form a hard and compact mass.

Concrete is a mixture of cement, sand, and crushed stone or gravel made into a paste with water. It sets in the course of a few days to a solid mass, which is much harder and has



By *Ewing Galloway*, N. Y.

Fig. 216. Reënforced-concrete bridge in process of construction.

greater strength than pure cement. Cement is never used alone but always as an ingredient of concrete. The latter has rapidly come to be one of the most important of building materials. It is used for making bridges, foundations, dams, walks, fences, and almost every sort of conceivable structure. When the concrete is to stand any severe tensile stress, as in the case of floors of buildings, steel rods or bands are embedded in it before it sets. This gives the mass much greater strength; such a material is called **reënforced concrete** (Fig. 216).

406. Other calcium compounds. Among the other important compounds of calcium are **bleaching powder** ($CaCl(OCl)$), **calcium carbide** (CaC_2), and **calcium cyanamide** ($CaCN_2$), all of which are prepared from lime. A product, called **calcium cyanide**, has recently been introduced as a fumigating material for orchards. This substance is a solid with the formula ($Ca(CN)_2 \cdot 2\,HCN$) which in the presence of moisture produces the deadly hydrocyanic acid (HCN). **Calcium chloride** ($CaCl_2$) is found in sea water and is also a by-product of the Solvay process. In granular anhydrous form it is very deliquescent and hence is used for drying gases. A saturated solution freezes at $-48°$ C.; it forms the brine in refrigerating appliances. **Calcium fluoride** (CaF_2) occurs naturally and is the chief source of fluorine compounds.

Most ***calcium compounds*** *give to a Bunsen flame an* ***orange color.***

Strontium and Barium Compounds

407. Strontium and barium occur in nature as sulfates and carbonates. Their compounds are much rarer than those of calcium and they find only a few limited uses. *Barium compounds color flames a* ***yellowish green*** and for this reason are used in the manufacture of fireworks.

Barium chloride is a crystalline solid, which is soluble in water. It is used in the laboratory as a test for sulfuric acid, barium sulfate being formed as a white precipitate:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2\,HCl$$

Barium sulfate occurs naturally as **barite,** a white mineral which is used in the manufacture of paint and in coating paper.

Strontium compounds color a flame ***bright red.*** The nitrate ($Sr(NO_3)_2$) is used as red fire in pyrotechnics.

SUMMARY OF CHAPTER XXXI

METALLIC MAGNESIUM is prepared by the electrolysis of fused magnesium salts. It is an active metal and unites with nitrogen. It burns with a very intense white light and is used in flash-light powders, fireworks, and in the alloy magnalium.

MAGNESIUM OXIDE is prepared by heating the carbonate. It is very infusible and is used for making fire bricks. Magnesium hydroxide is a white insoluble substance.

METALLIC CALCIUM is prepared by the electrolysis of fused calcium chloride. It slowly decomposes water at room temperature.

CALCIUM CARBONATE occurs in many forms, such as marble, limestone, and chalk. It is insoluble in pure water but soluble in water containing carbon dioxide, the *bicarbonate* being formed.

HARD WATER contains dissolved salts. If the dissolved material is calcium or magnesium bicarbonates, it can be thrown out of solution by boiling. This is called *temporary hardness.* Hardness which cannot be removed in this way is called *permanent hardness.*

Hard water forms a crust in boilers and *precipitates calcium* and *magnesium soaps* with soap solutions. Temporary hardness can be removed (1) by boiling or (2) by slaked lime. *Permanent hardness* can be removed by sodium carbonate. Sodium carbonate, ammonium hydroxide, and borax are used in the household for softening water. *Permutite* is used for softening water for industrial purposes.

LIME (calcium oxide) is made by heating calcium carbonate. Lime rapidly and energetically combines with water, forming calcium hydroxide (slaked lime). Calcium hydroxide is only slightly soluble in water.

MORTAR is a mixture of calcium hydroxide and sand. Plaster is a mixture of calcium hydroxide, sand, and hair.

CEMENT is a partially dehydrated mixture of limestone and clay. When mixed with water it sets to a hard mass. This setting is due to the hydration of certain silicates and calcium oxide. *Concrete* is a mixture of cement, sand, and gravel.

FLAME TESTS: *Calcium* compounds give an *orange* flame.
Strontium compounds give a *crimson* flame.
Barium compounds give a *greenish* flame.

Questions and Problems

1. What properties have the metals of this family in common?

2. Write the equation for the reaction of magnesium and dilute sulfuric acid.

3. How could you distinguish between Epsom salts and Glauber's salt?

4. In what two different ways could you obtain carbon dioxide from magnesite? Write the equations.

5. How could you show that the alkali metals are more active than the metals belonging to the family of alkaline earths?

6. What is the difficulty about using hard water in the household?

7. What are the consequences of using hard water in a steam boiler?

8. What are the results of using sea water in a ship's boiler?

9. What is the difference between air-slaked lime and limewater?

10. Why is it dangerous to let barrels of quicklime get wet?

11. Compare the hardening of mortar with the hardening of plaster of Paris.

12. Explain why air-slaked lime can be used to " sweeten " soil.

13. Could you use a barium hydroxide solution in place of limewater in testing for carbon dioxide?

14. Write the equation for making calcium hydroxide into calcium acid sulfite ($Ca(HSO_3)_2$).

15. How could you obtain barium sulfate from barium chloride?

16. How much quicklime could be made from one ton of limestone, which is 97% pure calcium carbonate?

17. What weight of water would be needed to slake the lime made in Problem 16?

18. How many liters of carbon dioxide at 18° C. and 75 cm. pressure could be obtained from 1 kilogram of calcium carbonate?

19. What volume of dilute sulfuric acid containing 13% H_2SO_4 (specific gravity 1.09) will be needed to react completely with 3 grams of magnesium?

20. A solution containing crystallized barium chloride ($BaCl_2 \cdot 2\,H_2O$) was mixed with enough potassium sulfate (K_2SO_4) to precipitate all the barium. If the precipitate, when carefully washed and dried, weighed 10.00 grams, how many grams of the crystallized barium chloride was used?

Topics for Further Study

Soft and hard water. Is the water used in your household soft? How easily does it lather with soap? Compare it with rain water. Does any precipitate form on the inside of the teakettle? How effective is washing soda in removing any hardness which you may find? Try some of the cleansing or soap powders recommended for use with hard water. How is water purified for industrial use? (Thorp and Lewis's *Outlines of Industrial Chemistry.*)

Materials of construction. Why is this sometimes called the age of concrete and steel? Classify from a chemical standpoint the materials used in building houses, factories, and office buildings. Which of these were developed early in the history of civilization? Which is the most recent in invention? (Howe's *Chemistry in the World's Work* and *Chemistry in Industry*, vol. 2.)

CHAPTER XXXII

ALUMINUM AND SILICON

Sand and clay. Natural aluminum compounds — manufacture of aluminum — properties and uses — thermite — alumina — aluminum hydroxide — alums — purification of water — clay — pottery and porcelain.

Silica — properties and uses — silicic acid and silicates — glass — silicon — carborundum.

408. Sand and clay. The two materials sand and clay not only compose the bulk of our soil but have from the earliest times been used by man in the development of civilization. Earthenware and porcelain have been made for centuries by baking the clay found in certain localities. Many centuries before the Christian era, the art of manufacturing glass from sand, sodium carbonate, and lime was discovered. Sand is the oxide of the nonmetal silicon; clay is a combination of this oxide with the oxide of the metal aluminum (aluminum silicate). Because of the abundance (Fig. 13) of the compounds of these two elements — one a nonmetal, the other a metal, — they were the natural starting point of man's first chemical achievements. It remained for an American in the nineteenth century (C. M. Hall) to show how one of the elements, aluminum, could be prepared cheaply. This discovery constituted still another advance in man's struggle with his environment.

To understand the chemistry of the transformation of clay and sand into useful products, we must study the two elements aluminum and silicon.

Aluminum

409. Natural compounds of aluminum. Although aluminum is the most abundant metallic element, it is found in nature

only in the form of compounds. In this connection it is interesting to note that the only metals which occur free in nature to any extent are those located in the middle of the long periods in the periodic table (page 305); for example, iron, copper, silver, gold. **Bauxite,** a hydrated oxide of aluminum, is the source of the metal and of most of its compounds. In Greenland a double fluoride of aluminum and sodium is found which is called **cryolite** ($AlF_3 \cdot 3\,NaF$). Aluminum is also found as a constituent of all the common siliceous rocks, such as feldspar, clay, mica, and slate. **Clay** is an aluminum silicate which is formed by the weathering of such rocks as feldspar. **Emery,** a very useful and valuable natural abrasive, is an impure form of aluminum oxide (Al_2O_3), colored brown by iron oxide. **Sapphires** and **rubies,** which are highly prized as gems, are beautifully crystallized aluminum oxide.

410. Manufacture of aluminum. Because of the very great chemical activity of the element, aluminum oxide cannot be reduced to metallic aluminum by means of carbon in a furnace. The metal is now obtained by the **electrolysis** of its oxide. The process was discovered by Hall in 1886. The electrolyte for this process is a solution of aluminum oxide in *fused* cryolite; the cryolite is not changed during the process but serves only as a solvent. The oxide must be very pure and is prepared from bauxite by a long and careful process of purification.

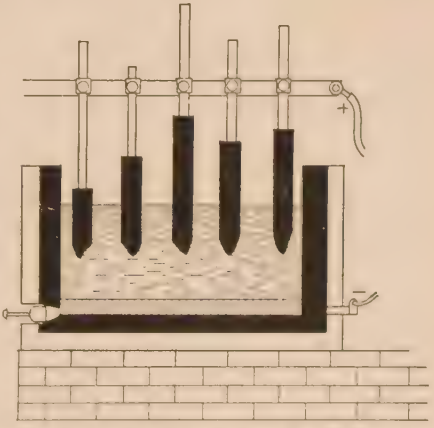


Fig. 217. Diagram illustrating the making of metallic aluminum.

The electrolysis is carried out in the apparatus shown in figure 217. An iron box is lined with amorphous carbon, which serves as the cathode. The anode is a set of carbon blocks suspended in the mixture. The cryolite is melted by the electric arcs which are formed when the current is first turned on. Aluminum oxide is added from time to time as the electrolysis proceeds. The metal is liberated at the cathode and collects as a liquid at the bottom of the box, from which it is drawn off into suitable molds. Oxygen is liberated at the anode and to a large extent burns up the carbon electrodes, which have to be renewed frequently. It requires only about 8 volts to keep the process going, but a current of several thousand amperes is needed.

411. Properties. Aluminum is a silver-white metal which usually has a rather dull surface due to a thin coating of the oxide. It is very light in weight, being only one-third as heavy as iron, and is an excellent conductor of both heat and electricity. It does not work well in a lathe and can be soldered only with difficulty.

Aluminum is a moderately active metal, but because of the thin coating of adhering oxide which is always present, it is not acted on by moist air, hot or cold water, or dilute sulfuric or nitric acids. Hydrochloric acid acts on it rather rapidly, producing hydrogen. It is dissolved by sodium or potassium hydroxide with the formation of compounds called **aluminates** and with the liberation of hydrogen:

$$6\ NaOH + 2\ Al \longrightarrow 2\ Na_3AlO_3 + 3\ H_2 \uparrow$$

412. Uses. Aluminum is not so cheap as steel, and its use is therefore restricted to articles in which lightness is a prime essential, such as parts of automobiles and airplanes. It is sometimes used in the place of copper as a conductor of electricity. It is a very satisfactory material for cooking utensils, not only because of its lightness, but also because *it keeps bright*, since the thin film of oxide is transparent and protects the metal from further action of the air. Powdered aluminum is used extensively as a paint to protect other metals from corrosion. Very thin foil made of aluminum is replacing tin foil to some extent.

There are many important alloys of aluminum. Copper containing 5 to 12 per cent of aluminum is called **aluminum bronze**; it has a brilliant golden-yellow color. **Magnalium** contains about 5 per cent of metallic magnesium. **Duralumin** contains about 4 per cent copper and 1 per cent of magnesium. These alloys can be worked more easily than the pure metal and are stronger. They have been much used in the manufacture of dirigibles and all-metal airplanes.

413. Thermite. Metallic aluminum is a very powerful reducing agent. It reacts with the oxides of many metals, producing aluminum oxide and the free metal. This reaction takes place with the evolution of much heat and when once started proceeds vigorously. A mixture of aluminum and iron oxide is called **thermite**. When this mixture is ignited by means of a burning strip of magnesium ribbon, a reaction takes place, and a temperature of 3000° to 3500° C. is reached:

$$2\ Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2\ Fe$$

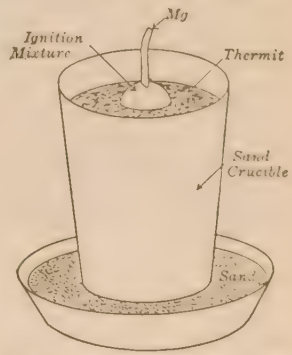


Fig. 218. Making molten iron by the use of thermite.

Some thermite is placed in a sand crucible and on top of it a little heap of the ignition mixture consisting of sodium peroxide and powdered aluminum. Into this heap is inserted a piece of magnesium ribbon (Fig. 218). The crucible is then set into a pan of sand, and the magnesium ribbon is ignited. So much heat is developed that great care must be taken in doing the experiment. Very soon the crucible will contain liquid iron at the bottom and the fused slag on top. This is a good example of an exothermic reaction.

Advantage is taken of this reaction in **welding** rails (Fig. 219), shafting, and similar objects. The reaction is carried out in a cone-shaped crucible with a bottom opening. Extremely hot molten iron collects at the bottom and is allowed to run out

on to the joint, which has been previously warmed to a red heat. The molten iron unites with the warm iron and makes a solid weld.

The same reaction enters into the preparation of **manganese** and **chromium** from their oxides. A mixture of powdered aluminum and the oxide is ignited; the free metal is thus produced.

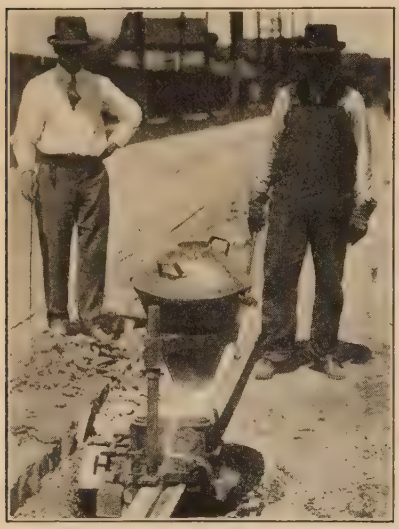


Fig. 219. Welding rails with thermite.

414. Alumina. Aluminum oxide, or **alumina** (Al_2O_3), has already been mentioned. As it occurs naturally in a variety of forms and is extremely hard, it is extensively used as an abrasive. **Corundum** and **emery** are natural forms of aluminum oxide which are thus employed. **Alundum,** an artificial abrasive, is prepared by heating the oxide obtained from bauxite in an electric furnace until it just melts. Crucibles and muffles are often made of alundum because of its extremely high melting point.

The colors of ruby and sapphire, both of which are natural crystallized aluminum oxide, are due to traces of impurity. Substances very similar to these are now prepared artificially by fusing aluminum oxide with a small amount of other metallic oxides to give the desired color; chromium compounds give the ruby color, and a trace of titanium gives the blue. These **artificial gems** are chemically identical with the natural ones and can be distinguished from them only with great difficulty. Their preparation forms a very large and profitable industry.

415. Aluminum hydroxide. The hydroxide is formed as a colloidal precipitate when ammonium hydroxide is added to a solution of a salt of aluminum:

$$6\ NH_4OH + Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3 \downarrow + 3(NH_4)_2SO_4$$

When heated, the aluminum hydroxide is decomposed into the oxide and water:

$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O \uparrow$$

Aluminum hydroxide has both ***acid*** *and* ***basic*** *properties.* This means that it ionizes in two different ways:

$$Al(OH)_3 \longrightarrow Al^{+++} + 3\ OH^-$$

$$H_3AlO_3 \longrightarrow 3\ H^+ + AlO_3^{---}$$

It dissolves in most acids to form soluble salts, and in the strong bases to form aluminates:

$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$$

$$Al(OH)_3 + 3\ NaOH \longrightarrow Na_3AlO_3 + 3\ H_2O$$

416. Alums. When a solution of aluminum sulfate is mixed with a solution of potassium sulfate and evaporated, a double salt crystallizes out, which has long been known as **alum** ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$).

We prepare a saturated solution of alum and suspend in it a small alum crystal by a thread, as shown in figure 220. The small crystal grows and often becomes very nearly perfect.

Fig. 220. Nursing crystals of alum.

This substance belongs to a class of compounds called **double salts.** We do not know the reason for their formation or for the way in which the atoms are joined together. There are a number of double salts which have the same crystalline form as ordinary,

or potassium, alum, and which have a similar formula: such as **ammonium alum** ($Al_2(SO_4)_3 \cdot (NH_4)_2SO_4.24\ H_2O$) and **chrome alum** ($K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$). It should be noted that the last substance is called an *alum although it contains no aluminum*. Ordinary alum is the commonest form in which aluminum compounds are used.

417. Water purification. When aluminum hydroxide is precipitated in muddy water, it has the power of carrying down with it suspended particles. This property is used to advantage in the purification of water. Alum and lime are added in proper proportions to the contaminated water supply; the aluminum hydroxide which is formed carries down the suspended material from the water.

418. Clay and bricks. The purest form of clay, known as **kaolin,** is an aluminum silicate. This is a white substance formed by the decomposition of feldspar rock under the influence of weather over a long period of time. Feldspar is a potassium aluminum silicate which is slowly converted into soluble potassium compounds and kaolin. Impure, or ordinary, clay is a mixture of kaolin with other substances, particularly iron compounds, which give it a red color.

Fig. 221. Filling a pottery oven with ware to be baked.

Bricks, tiling, flower pots, and similar porous stoneware are made of common clay. The clay is molded into the desired form and then baked in ovens fired generally with gas (Fig. 221). For many purposes the porous material must be covered with an impervious glaze. This is done by bringing salt into contact with the hot surface; a fusible sodium alumi-

num silicate is formed, which flows over it and on cooling solidifies to a hard mass. Drain pipes are made in this way. Clay containing a large amount of silica is used for preparing fire bricks, stove linings, and other materials which are to be subjected to a very high temperature.

419. Porcelain. The better grades of pottery, **porcelain** and **china**, are made from pure white kaolin, feldspar, and quartz. The materials are ground fine, mixed with water, and molded into the desired shape. This may be done by hand with the help of a potter's wheel, or the mixture may be poured into a mold of plaster of Paris. When dry, the object is baked at a relatively low temperature until it is firm and hard but still porous. It is then covered with a thin coating of feldspar and silica and heated at a higher temperature and for a longer time. The thin coating melts and forms a glaze; according to the length of time of heating and the composition of the material, the latter also partially melts and fuses with the glaze. In such articles the glaze and the body of the material are thus melted practically into one mass. Colored decorations are put on by adding colored oxide to the coating which subsequently becomes the glaze.

Silicon

420. Silica (SiO_2). The commonest compound of silicon is the oxide (SiO_2) called silicon dioxide, or more usually **silica**; sand, sandstone, and certain other substances which are found in enormous quantities consist of silica. Its purest form is quartz, or rock crystal, which occurs in fine, clear, six-sided prisms. Sometimes it appears in colored forms due to impurities; thus, *amethyst* is violet, *rose quartz* pink, *smoky quartz* brown, and *milky quartz* white. Other varieties of silica are onyx, opal, and flint. Petrified wood is a kind of silica which has gradually replaced the wood fiber of a tree, changing it to stone.

Silica is also found in plants, especially in the leaves and stems, where it appears to give rigidity. Certain one-celled

marine animals have skeletons containing silica. These animals belong to the **infusoria;** in some localities there are immense deposits of very fine sand called **infusorial earth** (Tripoli). This material is used to absorb nitroglycerin in making dynamite; also for removing coloring matters from oils and in making polishing powders.

421. Properties of silica. It is a hard, brittle substance and hence is used as an abrasive. **Sandpaper** consists of sharp

Fig. 222. Laboratory utensils made out of quartz.

quartz sand glued on paper. Silica can be melted in the oxyhydrogen flame and made into fine threads, tubes, flasks, or crucibles (Fig. 222).

Very recently by means of the electric furnace and by the use of high temperatures, high pressures, and high vacua, **clear fused quartz** has been produced on a commercial basis. It has a melting point of 1715° C., and its coefficient of expansion is the smallest of any known material. If we heat a quartz crucible red-hot in the flame of a blast lamp and then plunge it into cold water, it does not crack. It is probably the most transparent solid substance and the only one which can be produced in large amounts which will transmit ultra-violet rays. It is also remarkably transparent to low heat rays and is superior to

glass, porcelain, and similar material as an electrical insulator. Disks of clear, fused quartz have been polished so flat that no point in their surfaces differs by more than 2 ten-millionths of an inch from a true plane (Fig. 223).

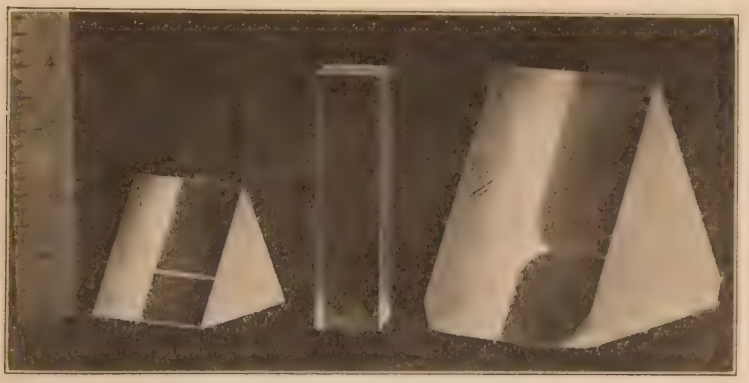


Fig. 223. Clear fused quartz for optical instruments.

Quartz vessels are not attacked by the common acids. However, they are dissolved very rapidly by hydrofluoric acid (H_2F_2). Silica also dissolves in fused alkalies to form **silicates:**

$$2\,NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

This reaction likewise takes place when silica is boiled with a concentrated alkali solution.

422. Silicic acid and silicates. Silicon dioxide is the anhydride of an acid with the formula H_2SiO_3 ($H_2O + SiO_2$); but this acid cannot be formed by dissolving silica in water. It is very weak and can be prepared only from its salts, the **silicates.** The silicates of calcium, magnesium, aluminum, and iron form the greater part of the earth's crust. Many of the common rocks, such as granite, are composed of minerals which are complicated and mixed silicates. Most of them are insoluble in water, but the alkali silicates are soluble.

Water glass, or sodium silicate (Na_2SiO_3), is made by fusing together silica and sodium carbonate:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$

A solution of sodium silicate is an excellent preservative for eggs since it fills the pores of the shells and thus makes them air-tight. It is used to render wood or cloth fireproof, and as a cement for glass and pottery. Silicic acid is precipitated when sodium silicate is acidified:

$$Na_2SiO_3 + 2\,HCl \longrightarrow H_2SiO_3\downarrow + 2\,NaCl$$

The acid comes down as a gelatinous precipitate containing a rather indefinite amount of water. When heated sufficiently, the jelly loses all of its water and forms silica. Silicic acid is a very good example of a colloid.

423. Glass. Common glass is made by melting together sand, sodium carbonate, and calcium carbonate. At a high temperature the carbonates react with the sand, forming glass, which is a mixture of sodium and calcium silicates:

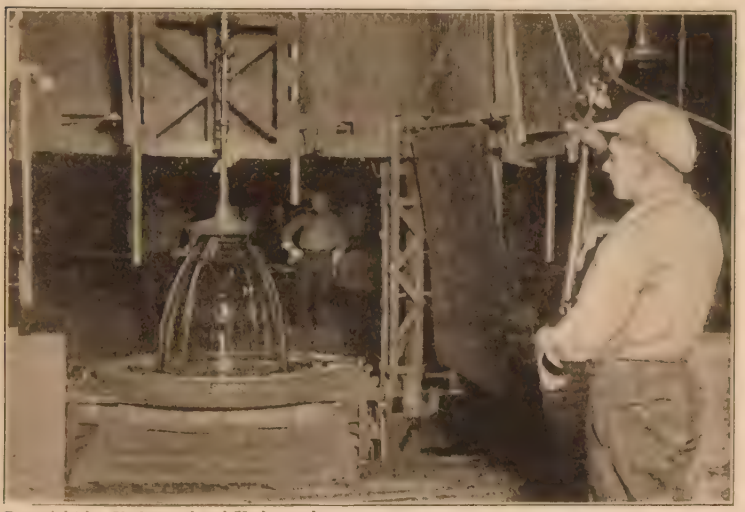
$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

Such a mixture of silicates solidifies on cooling but does not crystallize. It stays as a transparent amorphous mass which may be considered as a supercooled solution of the one silicate in the other. On long standing certain grades of glass begin to crystallize, and this results in an opaqueness and a fragility of the glass. Hard glass, which melts at a higher temperature than ordinary, or soft, glass, consists of a mixture of potassium and calcium silicates. Flint glass contains the silicates of lead, barium, and potassium. If part of the silica is replaced by the oxide of boron, the glass will contain borates, which have a very low coefficient of expansion. **Pyrex** glass is an example of a boro-silicate glass.

In the manufacture of glass the ingredients are heated in fire-clay pots or vats by gas flames to a very high temperature. All the carbon dioxide must be expelled from the melt, otherwise bubbles and streaks will occur in the product. Traces of metallic oxides added at this point produce different colors in the glass. The cheaper grades are often somewhat green because of iron oxide.

Glass is worked into shape by blowing. A mass of the fused glass is taken on the end of a long blowpipe, and a skilled workman blows



Copyright by *Underwood and Underwood.*

Fig. 224. Mechanical blowing of cylinders for window glass.

it into large cylinders or other desired shapes. Window glass is made from cylinders by cutting off the ends, slitting the cylinder lengthwise, and rolling it out as a plate while it is still soft. Recently a process has been devised by which a continuous sheet of glass can be pulled out of the vat. Mechanical blowers (Fig. 224) have now been introduced for making the larger cylinders. The apparatus automatically dips a large pipe into a kettle of molten glass, and then gradually raises it, pulling the molten glass upward as the pipe rises. A steady stream of air is kept flowing in through the pipe. Bottles and similar articles are formed by blowing the glass into molds either mechanically or by hand (Fig. 225). Plate glass is manufactured by pouring molten glass on a table, rolling it with a hot iron, and finally carefully polishing it.

Flint glass has peculiar optical properties and is used in the manufacture of lenses. Because of its brilliant appearance it is also made into ornaments, such as cut-glass vessels. The designs are cut by an emery wheel and then the object is polished with a very fine abrasive.

Copyright by *Keystone View Co.*

Fig. 225. Glass bottles are blown in a mold.

424. Silicon. This element is seldom seen because it is reduced from its compounds only with great difficulty. But silicon can be prepared by heating pure sand with carbon to a high temperature in an electric furnace:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO\uparrow$$

It occurs as **amorphous silicon,** a brown powder, and as **crystallized silicon** in black needles. Silicon is used as a deoxidizing agent in refining steel and in making iron alloys.

425. Carborundum. If the reaction between sand and carbon is carried out under certain conditions with a large excess of carbon, a compound of these two elements is formed, known as **carbon silicide,** or **carborundum.** An electric furnace (Fig. 226) similar to the one used in the manufacture of graphite is employed for this purpose. The core of the furnace is a mass of granulated coke. A mixture of sand, sawdust, coke,

and a little salt is piled around the central core. The heat generated by the passage of a strong current through the coke is sufficient to cause the reaction to take place in the surrounding mass.

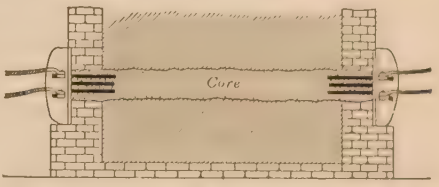


Fig. 226. Section of an electric furnace for making carborundum.

Carborundum is a crystalline solid with a beautiful purple color. It is extremely hard and is used as an abrasive in the form of grinding wheels and hones, and as a fine polishing powder.

SUMMARY OF CHAPTER XXXII

ALUMINUM occurs very extensively as oxides and silicates. The metal is made by electrolysis of the oxide dissolved in fused cryolite.

The metal is not attacked by moisture or air because of a thin coating of oxide. It dissolves in hydrochloric acid and in alkali solutions.

THERMITE is a mixture of iron oxide and metallic aluminum. When ignited, metallic iron is produced at a very high temperature. Thermite is used in welding.

ALUMINUM OXIDE (alumina) is used as an abrasive and in the preparation of artificial gems.

ALUMINUM HYDROXIDE is both acidic and basic. It forms salts with acids and aluminates with bases. Certain double salts of aluminum are called *alums*.

CLAY is essentially an aluminum silicate. It can be baked into a hard, porous form. A glaze can be put on by a suitable process.

SILICON is a very abundant element which belongs to the carbon family. It can be prepared by heating sand and carbon in an electric furnace. With an excess of carbon a carbon silicide, *carborundum*, is formed.

SILICA is silicon dioxide, which is widely distributed as sand. Laboratory apparatus can be made from fused silica. *Clear fused quartz* has been manufactured on a commercial scale, not only in the form of rods and tubes but also as blocks or slabs for optical instruments. Silica is dissolved by hydrofluoric acid and slowly by sodium hydroxide.

SILICATES are salts of silicic acid. This acid on heating decomposes into the oxide and water. The silicates are insoluble, except those of sodium and potassium.

GLASS is a mixture of silicates. It is an amorphous solid. Ordinary glass is a mixture of sodium and calcium silicates. Hard glass contains potassium silicates. Flint glass contains the silicates of lead, barium, and potassium.

Questions and Problems

1. What has made aluminum a comparatively cheap metal?
2. If aluminum is the most abundant metallic element, why is it not the cheapest metal?
3. Why does the price of aluminum depend on the cost of electricity?
4. What are the especial advantages of aluminum for kitchen utensils?
5. What are the advantages of the thermite method of welding over other methods?
6. What would be the reaction of a solution of aluminum sulfate on litmus? Explain.
7. Make a list of the metals prepared by electrolysis.
8. Write the equation for the reaction of aluminum on hydrochloric acid.
9. Write the equation for the hydrolysis of aluminum chloride.
10. Write the equation for the reaction of alum and lime ($Ca(OH)_2$).
11. Name five important uses for silica.
12. What is the difference between water glass and ordinary glass?
13. What advantages has quartz glass for chemical apparatus? What disadvantages?
14. Compare carbon and silicon.

15. Why is an ordinary window not so smooth as plate glass?

16. How would you expect a solution of water glass to react with litmus? Explain.

17. Why is it sometimes difficult to remove the ground-glass stoppers from bottles containing ammonium hydroxide?

18. What is the difference between silicon carbide and carbon silicide?

19. Name the ingredients of three different varieties of glass and give uses for each variety.

20. Compare aluminum oxide and silicon dioxide.

21. Make a list of the abrasives mentioned in this chapter and give the formula of each.

22. How many liters of hydrogen (standard conditions) could be generated by the action of hydrochloric acid on 1 kilogram of aluminum?

23. Calculate the percentage of water of crystallization in common alum.

24. Calculate the percentage of aluminum in mica ($KAlSiO_4$).

25. Find the simplest formula for the compound which contains 66.7% oxygen, 29.2% silicon, and 4.10% hydrogen.

26. How much commercial caustic soda (10% water) would be needed to prepare 100 pounds of water glass?

Topics for Further Study

Glass and pottery. A number of industries and arts were developed long before the beginnings of the science of chemistry. Skilled craftsmen found by experience methods of producing such substances as glass and pottery. What chemical principles have recently been applied to these industries to bring about great improvements and economies? (Duncan's *Chemistry of Commerce*, *Chemistry in Industry*, vols. 1 and 2 and Findlay's *Chemistry in the Service of Mankind*.)

Products of the electric furnace. What substances are now manufactured with the aid of the electric furnace? Would it have been possible to produce these materials before the electric generator was invented? How does this use of the electric current differ from that in the production of sodium hydroxide and chlorine or metallic aluminum? (Duncan's *Chemistry of Commerce*, Slosson's *Creative Chemistry*, Cressy's *Discoveries and Inventions*, *Chemistry in Industry*, vol. 1, and J. C. Philip's *Romance of Modern Chemistry*.)

CHAPTER XXXIII

IRON AND STEEL

Iron ores — smelting — blast furnace — cast iron — wrought iron — steel — microscopic study of iron — crucible steel — Bessemer steel — open-hearth process — electric furnace — hardening and tempering of steel — case hardening — special steels and iron alloys — comparison of irons and steels.

426. Importance of iron. Iron is doubtless the most valuable metal in the world. Not that it is so costly; indeed, its value rests upon its cheapness and its adaptability to an enormous number of uses. It has in fact become a necessity in our modern life, and we are said to live in **the age of steel and concrete.** Particularly in our own country has the industry of iron and steel production reached such huge proportions that *the yearly output approximates thirty million tons.* For the development and control of this industry chemical knowledge and engineering have been required. In our present chapter we shall discuss methods of iron and steel production.

" In recent years the introduction of manganese, chromium, and tungsten into steel has made modern machinery possible. Manganese has been the ' leavening agent ' of steel and has given low-carbon steel strength and forgeability. Nickel, vanadium and molybdenum have given steel the necessary wide elastic limit and great toughness to withstand the terrific vibration of light automotive machinery."* Thus we see that we are even now passing from the age of steel to an " age of alloys."

* From H. E. Howe's *Chemistry in the World's Work.* D. Van Nostrand Co., 1926.

427. Iron ores. The principal compounds of iron which occur naturally are various forms of the oxide, the carbonate, and the sulfide. Of these the oxides are the chief source of metallic iron. The most important **iron ores** are hæmatite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3 \cdot 3\,H_2O$), and siderite ($FeCO_3$).

Metallic iron is obtained from these oxides by the action of carbon and carbon monoxide at a high temperature. The production of a metal from its ores is often called **smelting.** Iron ore is never pure iron oxide but always contains certain amounts of other mineral matter, such as quartz or limestone. For this reason the smelting must be done in such a way that these impurities can be conveniently removed.

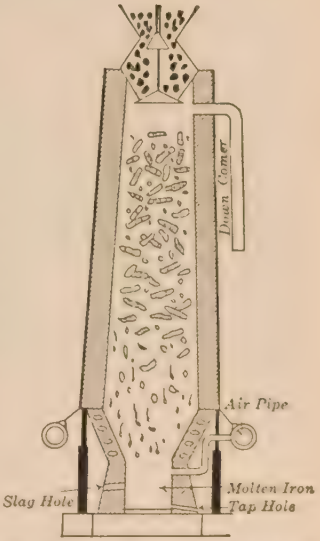


Fig. 227. Diagram of a blast furnace.

428. The blast furnace. The production of iron from its ores is carried on in an apparatus called a **blast furnace.** It consists of an iron structure 60 to 90 feet high lined with fire brick (Fig. 227). Near the bottom of the furnace are a number of pipes called **tuyeres,** which allow a stream of hot air to be blown into the furnace. This air is usually dried by first cooling it to a low temperature, the water condensing out in the form of ice. Before the dry air enters the furnace it is preheated by means of the so-called **stoves,** shown as towers in the picture (Fig. 228). *The charge consists of a mixture of the* ***ore, coke,*** *and a substance called a* ***flux.*** The purpose of the flux is to combine with the rocky impurities in the ore. When the impurity is mostly silica, the flux is limestone; if the impurity is limestone, the flux is silica. The resulting compound in either case is calcium silicate and is called slag. The slag melts at a lower temperature than either the impurities or the flux, and this causes the whole mass to begin to soften at a relatively lower temperature; hence

the name flux (a flowing). The heat required for the process is generated by the combustion of the coke in the lower half of the furnace. Carbon dioxide is first formed but is immediately reduced to carbon

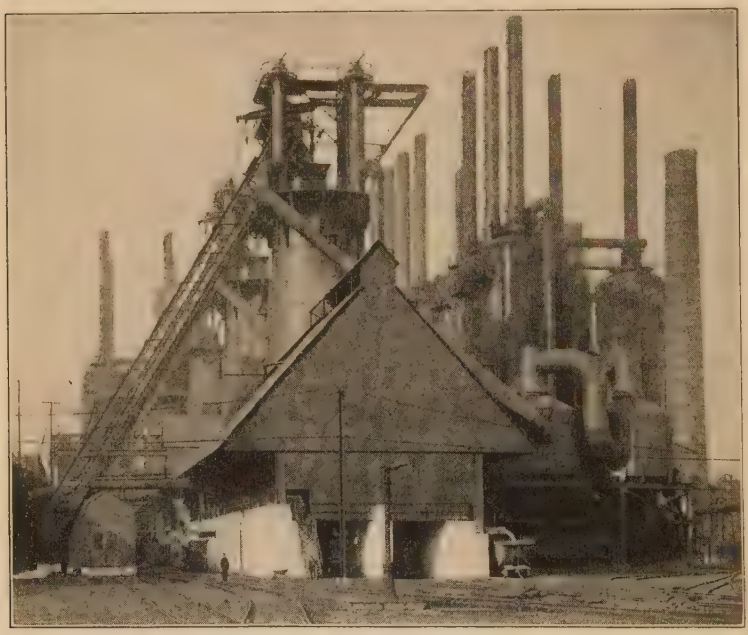


Fig. 228. Blast furnace and its stoves.

monoxide by the red-hot coke. Carbon monoxide ascends and meets the iron oxide in the upper half of the furnace and there reduces it to iron:

$$Fe_2O_3 + 3\,CO \rightleftharpoons 2\,Fe + 3\,CO_2$$

This reaction is reversible, and it is necessary to have an excess of carbon monoxide in order to carry it through. Therefore the gases which escape contain 20 to 35 per cent of carbon monoxide. They are combustible and are burned in the stoves which preheat the incoming air.

The charge is fed in through the hopper at the top and slowly descends through the furnace. The iron and slag begin to melt and flow when they reach the lower part of the furnace. The complete reduction of iron oxide then takes place by means of hot carbon:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$

The slag and the molten iron form two layers; the latter, being heavier, is at the bottom. The furnace is tapped from time to time at the proper points, and the iron and slag are separately run off. A blast furnace is kept in continual operation; it is not necessary to interrupt it until the lining has been worn out. Figure 229 shows by a diagram what *goes into* the furnace and what *comes out*.

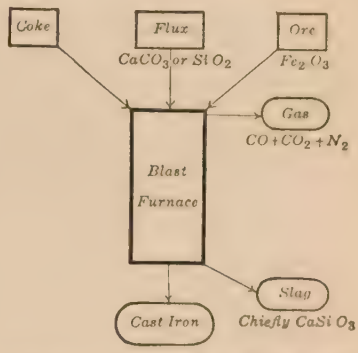


Fig. 229. Diagram showing what goes into and what comes out of a blast furnace.

429. Cast iron. The molten iron from the blast furnace is run into sand molds or a continuous belt carrying iron molds; the resulting metal is called **cast iron** or **pig iron.** It is impure metallic iron and contains about 5 or 6 per cent of impurities including silicon, manganese, sulfur, phosphorus, and carbon. The latter is present in relatively large amounts, varying from 3 to 5.5 per cent. The other impurities exist in less amounts. Pure iron melts at 1510° C., but because of the presence of the impurities cast iron melts at about 1100° C. Pig iron can therefore be easily remelted and cast into any desired form. It expands on solidifying, and consequently the metal fills all the details of the mold and makes a very satisfactory casting. It is, however, brittle and has a rather low tensile strength. It cannot be welded. It is used for making such things as stoves, radiators, ornamental iron work, base plates, and other heavy parts of machines.

430. Wrought iron. Most of the impurities in cast iron can be removed by heating pig iron in contact with iron ore. This is done in a **reverberatory furnace** (Fig. 230). The hot products of combustion, which are deflected by the low roof, play upon the pig iron and melt it. Workmen with long rods stir the molten iron on a bed of iron ore and in this way bring it thoroughly into contact with the oxide, which in turn oxidizes the carbon and sulfur to volatile oxides. The phosphorus

and silicon are oxidized, and these oxides combine with lime or some other basic oxide which is present and form a slag. As the impurities are extracted from the iron, its melting point rises and it becomes thicker and thicker. Finally it is removed in balls on the ends of the iron rods. While still hot these balls are pressed out into bars, and the product is known as **wrought iron.**

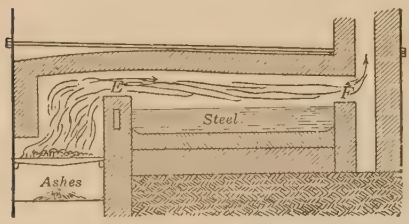
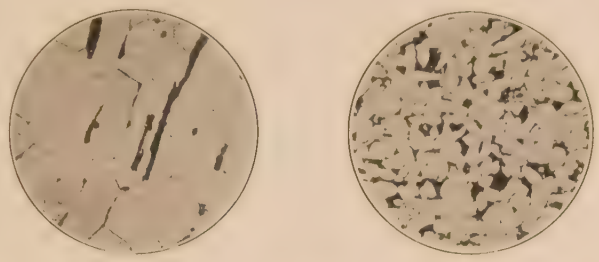


Fig. 230. Diagram of reverberatory furnace.

Wrought iron is a fairly pure iron (table on page 419) except for the small amounts of slag which always remain in it and give to it its fibrous structure. It is extremely tough and hence is used in the manufacture of articles such as anchors and chains, which must stand severe and sudden stresses. It is not brittle and can readily be welded.

431. Steel. The amount of carbon in iron greatly influences its properties. It is probably present in the form of a compound called **iron carbide,** or **cementite** (Fe_3C). Wrought iron contains less than 0.2 per cent of carbon; cast iron, as we have seen, from 3 to 5.5 per cent. Between these extremes lie materials which are called steel and which contain usually between 0.60 and 1.5 per cent of carbon. As a matter of fact, considerable steel (called **mild steel**) is now manufactured which, as far as its carbon content is concerned (less than 0.2 per cent), is not different from wrought iron. Steel is more uniform and freer from slag than wrought iron. It also has a greater tensile strength. Wrought iron is always hammered out into the desired shape, whereas steel is first poured into a mold and the ingot is subsequently given a mechanical treatment, generally while still hot. In contrast with cast iron, steel is malleable and can be forged and rolled; as a rule, it is not brittle and can be welded. Steel containing more than about 0.5 per cent of carbon can be hardened and tempered in such a way that it becomes very hard and brittle; wrought iron, cast iron, and mild steel cannot be hardened.

Microscopic study of iron and steel. In recent years the microscope has been used to study the structure of metals. When a specimen of iron or steel is polished and then suitably etched with weak acids, it is possible *to detect certain characteristic crystalline formations* under the microscope. Figure 231 shows such microphotographs of wrought



1 *2*

Fig. 231. Microphotographs of wrought iron (1) and soft steel (2).

iron and soft steel. This study is known as **metallography**, and has already been the means of discovering a close relationship between the microstructure and the physical properties of metals.

432. Crucible steel. Small quantities of steel of a high quality are made by melting together in clay crucibles a mixture of iron and small amounts of iron oxide or charcoal. The iron which is taken for this purpose is usually scrap steel, wrought iron, and occasionally some very pure pig iron. If there is more carbon in the iron than is desired in the steel, a small amount of iron oxide may be added to oxidize part of it to carbon monoxide, which escapes. If, on the other hand, the iron is too low in carbon, charcoal is put into the mixture at the start. In making crucible steel it is possible to add any given substance to the melt in order that the desired product will be obtained. This process is essentially a simple mixing and melting together of the required ingredients; *relatively pure iron, however, must be used in the process.*

433. Bessemer steel. To convert ordinary cast iron into steel we must remove a large amount of the impurities. This can be done by the Bessemer process.

In this process an apparatus called a **converter** (Fig. 232) is employed; this is made of steel and is usually lined with silica brick. It has a false bottom so that a stream of air can be introduced. The melted pig iron is run into such a converter, which holds about 15 tons, and air is blown through the molten mass. The carbon, silicon, and manganese are oxidized, and the heat of this oxidation is sufficient to keep the mass fluid. The impurities are oxidized first, and the process is stopped as soon as the character of the flame shows that all the carbon has been burned away. The desired amount of carbon (usually in the form of a high-carbon iron alloy) is now added. The converter is then tilted, and the material run out into ladles. The fluid steel is poured into iron molds, the slag, which floats, being left in the ladle. For making bar steel, steel wire, rods, and rails, the steel ingots are usually hexagonal blocks. These ingots while still red-hot are hammered or rolled out into bars and other desired objects (Fig. 233).

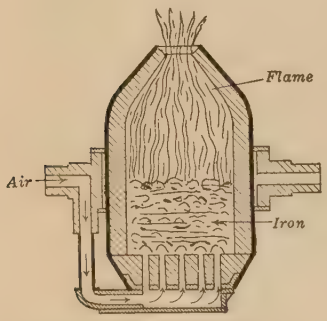


Fig. 232. Section of a Bessemer converter.

Sulfur and phosphorus are not removed from the pig iron by this process. Both of these substances, even in small amounts, are very deleterious to steel. Phosphorus causes it to be brittle at ordinary temperatures; sulfur has the same effect while it is being worked at a red heat. If pig iron containing very much phosphorus is used in the Bessemer process, the converter must be lined with dolomite ($CaCO_3 \cdot MgCO_3$). This is a basic lining, whence the process is termed the **basic Bessemer**; with the silica lining it is called the **acid Bessemer.** Under basic conditions phosphorus is removed as it is oxidized to the oxide, which then combines with the basic lining, forming calcium phosphate.

434. Open-hearth process. The open-hearth process for making steel has now been widely adopted for pig iron, which contains too much phosphorus for the acid Bessemer process.

The product is more uniform than that obtained by the Bessemer process as the reaction is slower and better controlled.

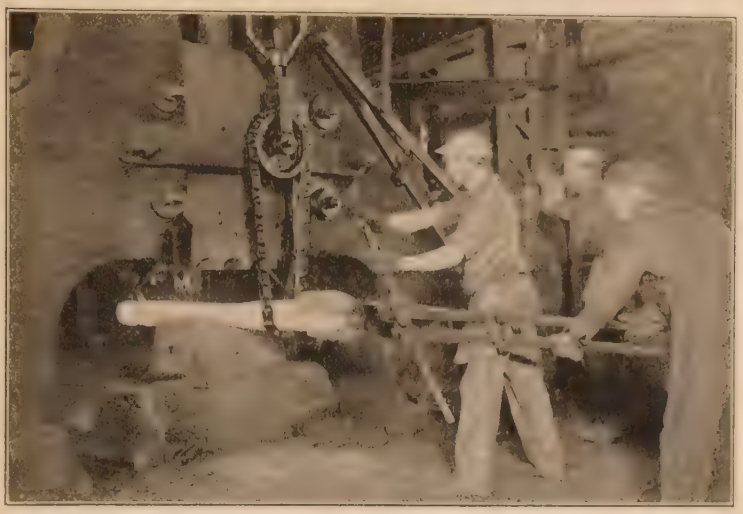


Fig. 233. Forging an axle with a hydraulic press.

Here the pig iron and iron oxide, together with some flux, are heated by a flame of producer gas in the furnace shown in figure 234. In order to get the high temperature necessary to melt steel, a regenerative device has been employed. By its means the fuel gas and the air are preheated as they pass through some brick work, which itself has been previously heated by the effluent gases from the furnace.

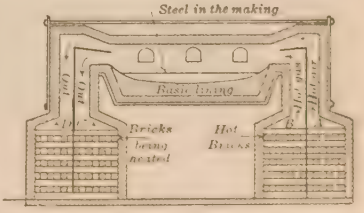


Fig. 234. Diagram of an open-hearth furnace.

The lining of the furnace may be either silica or dolomite, the processes being called the acid open-hearth and the basic open-hearth respectively.

The charge consists of pig iron (often mixed with scrap steel), iron oxide, and lime. The carbon content of the pig iron is reduced by the action of the iron oxide:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$

The iron oxide is added from time to time, and the molten mass " boils " with the evolution of carbon monoxide. The phosphorus and silicon are oxidized and pass into the slag by combining with the lime. This slag floats on top of the molten steel and protects it from the action of the hot flame, which would otherwise tend to oxidize the iron. The

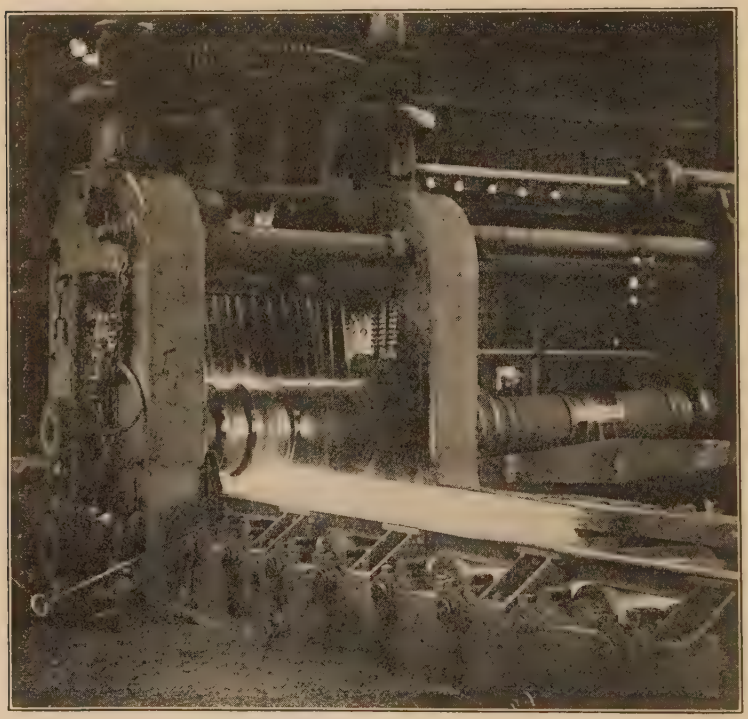


Fig. 235. Rolling mill making steel ingots into rails.

molten steel is tapped off in large ladles and poured into ingot molds. These steel ingots while still hot are rolled (Fig. 235) into rails, girders, and plates.

Molten steel dissolves considerable quantities of carbon monoxide and other gases, which it liberates on cooling, causing a porous structure. The addition of small amounts of strong

reducing agents to the melt just before it is poured helps to remove the dissolved gases and to give sounder ingots. Metallic silicon (or ferro-silicon, an alloy of iron), ferro-titanium, and ferro-manganese are often employed, as is also metallic aluminum.

435. Electric furnaces. The production of steel in electric furnaces has been developed to some extent and seems to have certain advantages. In one type of furnace, called the **Heroult** (Fig. 236), the heat is generated by the arcs between the carbon electrode and the molten metal. The reactions which take place in electric furnaces are much like those in the open hearth. They are always lined with a basic material and therefore readily remove phosphorus. Sulfur can pass into the slag only under reducing conditions. No strong oxidizing flame is present in an electric furnace as in an open-hearth furnace, therefore sulfur can also be eliminated. The electric furnace enables one to obtain a high temperature in a basic furnace without oxidation. For these reasons it is used for purifying steels made from low-grade pig iron and scrap.

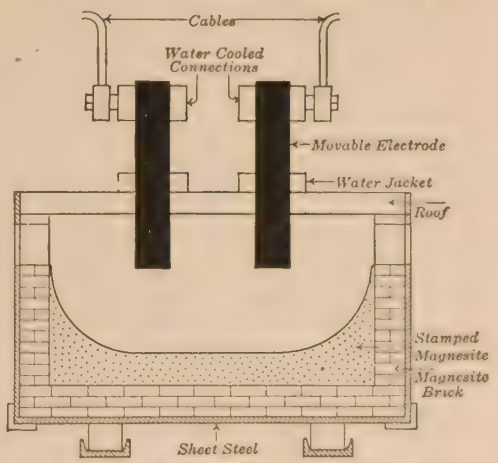


Fig. 236. Diagram of an electric furnace.

436. Tempering of steel. The carbon in steel is present as iron carbide. On cooling, a piece of steel passes through a number of rather complicated transformations at a temperature of 770° to 700° C. This range of temperature is called the

critical range; the transformations that take place involve the change of several allotropic forms of iron and the separation of iron carbide.

If the steel is slowly cooled through this range, the iron finally ends up as the alpha modification, and the iron carbide separates out in a certain crystalline condition. The resulting steel is comparatively soft. If steel containing more than 0.50 per cent of carbon is quickly cooled (quenched in water or oil) from above its critical temperature, the transformations taking place through the critical range are checked, and the resulting iron and iron carbide are left in such a form that a very hard, brittle steel is produced. Such steel is said to be **hardened**; the degree of hardness which results from the cooling depends somewhat on the carbon content of the steel. This steel is usually too brittle for most purposes and can be softened to varying degrees by heating to certain temperatures and then again quickly cooling. This process is called **tempering.** The higher the temperature to which we heat the steel in the tempering process, the more *the arrested transformations of the critical range can complete themselves* and the softer the steel will be. The temperature can be estimated by the play of colors which appear when the metal is heated. This is due to the formation of thin layers of iron oxides. The following table shows the colors and temperatures for tempering various articles of commerce.

Temperatures	Color of Oxide Film	Various Tools
225°–235° C.	Straw	Light turning tools
236°–250° C.	Yellow-brown	Screw-cutting dies and taps
251°–275° C.	Purple	Twist drills
276°–300° C.	Blue	Saws and wood-working tools.

The yellow tints give very hard but brittle steels, while the blue give softer and tougher steels.

437. Case hardening. If wrought iron or mild steel is heated in contact with powdered charcoal, it slowly takes up carbon. The carbon seems to penetrate the entire mass by degrees. This was the old **cementation process** of manufacturing what was known as **blister steel.** The same method, called **case**

hardening, is now employed for producing a layer of high-carbon steel on a body of the softer metal. Such a steel on being properly hardened and tempered has a hard exterior and a tough interior. This process is used to give the desired hard surface to various parts of machinery, such as automobile gears; a similar method enters into the manufacture of armor plate.

438. Special steels and iron alloys. A number of so-called special steels have become of importance for certain distinct purposes. These materials are manufactured by the open-hearth or crucible process. Steel containing from 7 to 20 per cent of manganese is exceedingly tough and resistant to wear. It cannot be machined. It is used for making rock-crushing machinery, safes, and brake shoes. **Chromium and nickel steels,** in which a few per cent of one or both elements are present, have great tensile strength and are very suitable for making parts for automobiles. They have considerable elasticity and therefore conform to the stress in such objects as springs, frames, and axles. **Stainless steel** contains from 12 to 14 per cent of chromium. It is made in small quantities for the manufacture of cutlery. A steel containing 36 per cent of nickel is called **invar**; it is properly not a steel at all but an iron alloy. It has practically no *coefficient of expansion* and is therefore very valuable in the manufacture of scientific apparatus; pendulums are often constructed of it. An alloy of iron and nickel containing 46 per cent of the latter is called **platinite**; it has the same coefficient of expansion as platinum and is used instead of this metal for "sealing in wires" in electric-light bulbs.

COMPARISON OF IRONS AND STEELS

	PER CENT OF CARBON	STRUCTURE	HARDNESS	USES
Wrought iron	0.05–0.2	Fibrous	Soft	Wire, water and steam pipes, horseshoes, rivets.
Steel (low-carbon)	0.05–0.8	Granular	Moderately soft	Structural steel, shafts, axles, nails.
Steel (high-carbon)	0.8–1.6	Granular	Hard, if tempered	Tools, springs, permanent magnets.
Cast iron	3–5.5	Crystalline	Brittle	Castings, bases, and columns.

Steels containing a considerable quantity of tungsten or molybdenum as well as chromium are called **high-speed steels.** They can be hardened and do not lose their hardness even when heated to a low red heat. For this reason they can be used on a lathe or similar machine at a high speed. The tools will cut while they are dull red. An element called **vanadium** when added in small amounts to certain special steels seems to be of great benefit. **Chromium-vanadium** steels and **chromium-nickel-vanadium** steels are used in the automobile industry.

SUMMARY OF CHAPTER XXXIII

THE PRINCIPAL IRON ORES are oxides. These are reduced to metallic iron by carbon and carbon monoxide in a blast furnace. A flux is added which combines with the rocky impurities to form a slag.

THE PRODUCT FROM THE BLAST FURNACE is *cast iron.* It contains 5 to 6 per cent of impurities, mostly carbon.

WROUGHT IRON is fairly pure iron except for mechanically held slag. It is made by heating cast iron in a reverberatory furnace on a bed of iron oxide. It can be welded and is malleable.

STEEL usually contains more carbon than wrought iron and less than cast iron. It can be cast and is malleable. It can also be welded. Low-carbon steel is very much like wrought iron; high-carbon steel can be hardened.

STEEL IS MADE in the *crucible process* from scrap steel and wrought iron, or very pure pig iron. *Steel* can be made from cast iron by (1) the Bessemer process, (2) the open-hearth process, (3) the electric furnace.

In the *Bessemer* process the molten metal is oxidized with air, the silica, carbon, and manganese being oxidized before the iron.

The basic open-hearth is the usual process for handling phosphorus pig. The oxidation is carried out by an oxide, the heat being supplied by gas flames. Phosphorus is satisfactorily removed, sulfur is lowered somewhat.

The electric furnace, used for refining steel, gives a high temperature without an oxidizing flame. Phosphorus, sulfur, and other impurities are removed in it.

THE HARDENING OF STEEL containing more than about 0.50 per cent of carbon can be done by heating above 700°–770° C., called the *critical range.* If the changes through this range are arrested by sudden cooling, a very hard steel results. This can be softened, or *tempered,* by reheating; the higher the temperature of reheating the softer the steel becomes. A layer of high-carbon steel can be put on a mild steel by *case hardening.*

SPECIAL STEELS: *Manganese steel* is very tough. *Chromium and nickel steels* are strong and somewhat elastic. They are used in making automobile parts. *Invar,* an iron-nickel alloy, has no coefficient of expansion. *Platinite* (46 per cent of nickel) has the same coefficient of expansion as platinum. *High-speed steels* can be hardened and used for tools cutting at a high speed.

Questions and Problems

1. Why is a blast furnace kept in continuous operation?
2. What *four* materials must be supplied to a blast furnace?
3. What use has recently been found for slag?
4. Why is iron pyrite never put into a blast furnace?
5. Why are the chemical changes carried on in a Bessemer converter difficult to control?
6. Why is the air forced into a blast furnace dried and preheated?
7. What keeps the iron hot in a Bessemer converter?
8. Why is steel made by the open-hearth process generally superior to that made by the Bessemer process?
9. What kind of iron is used to make stoves? chains? hammers? chisels? bridges? safes?
10. What is the purpose of adding ferro-manganese to the melt in making steel?
11. Which kind of steel is most easily welded? Why?

12. What is meant by the " critical range " of temperature in the heat treatment of steel?

13. Why is it more efficient to use " high-speed " tool steel than ordinary tool steel?

14. What determines the physical properties of steel besides its chemical composition?

15. Name four special steels and give two uses to which each is adapted.

16. What advantages has the electric furnace over other forms of furnaces for making steel?

17. Calculate the percentage of iron in each of these ores: (*a*) hæmatite; (*b*) magnetite; (*c*) limonite; and (*d*) siderite.

18. An iron ore contains 5% calcium carbonate. How many tons of sand must be added to remove all this calcium as slag in 100 tons of ore?

19. A certain iron ore was found by analysis to contain 61.59% of metallic iron. What per cent of ferric oxide (Fe_2O_3) does this represent?

20. How many tons of coke (98% carbon) will be needed to reduce 100 tons of iron ore which contains 88% ferric oxide (Fe_2O_3)?

Topic for Further Study

Special steels, their uses and manufacture. What is meant by the " heat treatment " of steel? (Slosson's *Creative Chemistry*, *Chemistry in Industry*, vol. 1, and Spring's *Non-Technical Chats on Iron and Steel*.)

CHAPTER XXXIV

THE IRON FAMILY

Pure iron — iron chlorides — ferrous and ferric compounds — oxidation and reduction — hydroxides of iron — iron oxides — other iron compounds — ferrocyanides — ferricyanides — blue prints — inks.

Cobalt and nickel — properties and uses of the metals — typical compounds.

Having discussed the preparation, properties, and uses of iron and steel, we shall now consider iron as an element and shall describe some of its compounds. **Iron, cobalt,** and **nickel** are neighboring elements in the eighth group of the periodic system. They occur in the middle of the first long period and have metallic properties; but they differ from such elements as sodium and potassium in their relative inactivity and the fact that their hydroxides are weak bases.

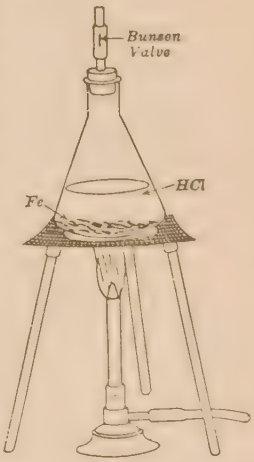


Fig. 237. Preparation of ferrous chloride.

439. Pure iron. Chemically pure iron can be made by the reduction of an iron salt with hydrogen. It has a white, metallic appearance and melts at about 1500° C. It is magnetic. Pure iron is not a very active metal and is not affected by cold water. It will decompose steam with the formation of iron oxide and hydrogen (§ 36). It readily displaces hydrogen from dilute acids (Fig. 237). If heated sufficiently it will burn in oxygen with the formation of the oxide (Fe_2O_3).

440. Iron chlorides. When iron is dissolved in hydrochloric acid in the absence of air, a compound called **ferrous chloride** ($FeCl_2$) is formed:

$$Fe + 2\,HCl \longrightarrow FeCl_2 + H_2 \uparrow$$

The escaping gas generally has an offensive odor due to certain impurities in ordinary iron. When hot iron reacts with chlorine gas, a dark brown solid known as **ferric chloride** ($FeCl_3$) is formed. The same compound is formed in solution when iron is dissolved in aqua regia. Both chlorides of iron are soluble in water and are used in the laboratory.

441. Ferrous and ferric compounds. Iron is an element which easily forms two series of compounds; in one of these it has a valence of **two** and in the other a valence of **three.** *Compounds in which iron is divalent are called* ***ferrous compounds*** *and those in which it is trivalent are called* ***ferric compounds.*** The chlorides just mentioned are typical examples of these two series of salts. Ferrous chloride in water gives the ferrous ion (Fe^{++}), and ferric chloride the ferric ion (Fe^{+++}).

Ferrous and ferric compounds may very readily be transformed into each other. If we treat ferrous chloride with a solution of chlorine water, it is turned into ferric chloride according to the equation

$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3$$

On the other hand, if we boil ferric chloride solution with iron filings, ferrous chloride is formed:

$$2\,FeCl_3 + Fe \longrightarrow 3\,FeCl_2$$

442. Oxidation and reduction. The change from ferrous to ferric compounds is called **oxidation.** The reverse change is called **reduction.** We have previously used these two words only when oxygen was involved in a reaction, but we shall now see that their meaning can be amplified. When carbon mon-

oxide burns, it takes up one more atom of oxygen, *increasing its valence from two to four. This is an oxidation reaction.* Carbon is the positive element in carbon monoxide. *Any increase in the valence of a positive element is* **oxidation;** *any decrease in the valence of such an element is* **reduction.** It is not necessary that oxygen be the negative element which is added to the compound in order to increase its valence. In the case of iron chloride the addition of one chlorine atom to ferrous chloride produces ferric chloride; and this reaction is *exactly parallel to the addition of an oxygen atom to carbon monoxide. it is oxidation.* It will be well to bear in mind this new definition of oxidation and reduction.

While the oxidation and reduction of iron compounds can take place without the action of oxygen, it often happens that we employ oxygen indirectly for this purpose. For example, *hydrogen peroxide* will quickly *oxidize* a hydrochloric acid solution of ferrous chloride to ferric chloride:

$$2\,FeCl_2 + 2\,HCl + [O] \longrightarrow 2\,FeCl_3 + H_2O$$
$$(H_2O_2)$$

Hydrogen sulfide will *reduce* ferric chloride to ferrous chloride; the hydrogen takes chlorine from the ferric chloride and leaves sulfur free:

$$2\,FeCl_3 + H_2S \longrightarrow 2\,FeCl_2 + 2\,HCl + S\downarrow$$

As far as the oxidation and reduction of ions is concerned, it is evident that oxidation is the removal of electrons, reduction the addition of electrons. Thus, in the reduction of the ferric ion (Fe^{+++}) one electron is added and the positive charge lowered to two (Fe^{++}).

443. Iron hydroxides. The addition of a base to a solution of a ferric salt gives a reddish brown precipitate of **ferric hydroxide:**

$$FeCl_3 + 3\,NaOH \longrightarrow Fe(OH)_3\downarrow + 3\,NaCl$$

Ferrous hydroxide ($Fe(OH)_2$) can be similarly precipitated from a ferrous salt. It is a white substance which is quickly

oxidized by the air, turns green and finally brown, and becomes ferric hydroxide.

When ferric hydroxide is heated to a red heat, it is converted into **ferric oxide** and water:

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$

Rust is the material which forms on the surface of iron when it is exposed to moist air. It is probably a mixture of ferric oxide and hydroxide. Its formation is hastened by the presence in the air of carbonic acid and other acid substances which help to dissolve some of the iron. Unlike the oxide of aluminum, rust does not adhere to the metal but keeps peeling off, exposing new portions to the action. For this reason a piece of iron will eventually turn completely to rust. Different grades of iron and steel rust at very different rates, and several schemes have been developed for protecting the metal from this action. Oil is used to keep tools from rusting because, although oxygen penetrates the oil, *moisture does not.*

444. Iron oxides. We have already seen that **ferric oxide** (Fe_2O_3) is the most important ore of iron. It occurs in great deposits, especially in northern Minnesota (Fig. 238). In the laboratory it can easily be prepared by heating ferric hydroxide or other ferric compounds.

Magnetic oxide of iron (Fe_3O_4) also occurs naturally. It is found in the form of a mineral known as magnetite or **lodestone,** which has magnetic properties. This is the oxide which is produced when steam acts on hot iron. It is a black material and can be made in such a way that it will firmly adhere to iron. A film of this oxide prevents rusting, and iron thus coated is known as Russia iron. It is used for locomotive boilers.

445. Other iron compounds. **Ferrous sulfide** (FeS) is formed when ammonium sulfide ($(NH_4)_2S$) is added to a ferrous salt. It is a black, insoluble compound. It is often used as a source of hydrogen sul-

fide. Another sulfide of iron is called **iron pyrite** (fool's gold) and has the formula FeS_2; it occurs abundantly in nature. It is sometimes used as a source of sulfur dioxide, since, when it burns, it forms sulfur dioxide and iron oxide.

Ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$), called **green vitriol** or **copperas**, is a common compound of iron and is often used in the industries and the laboratory when a soluble iron compound is desired.

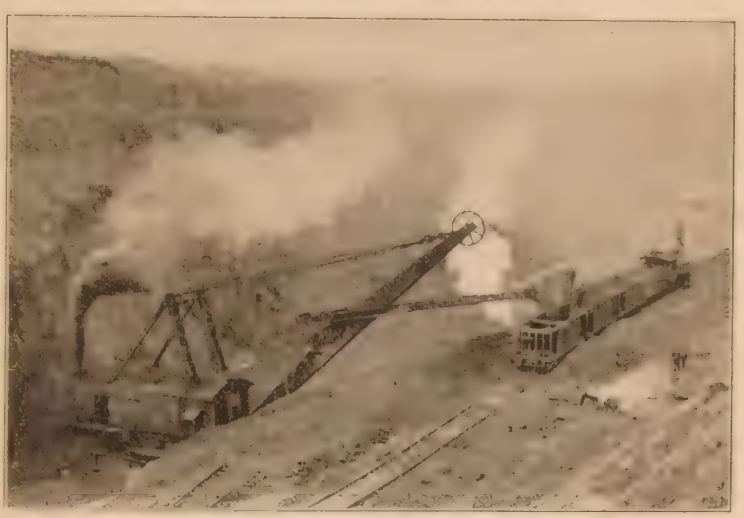


Fig. 238. Digging iron ore in Minnesota with a steam shovel.

Ferrocyanides. Potassium ferrocyanide ($K_4Fe(CN)_6$) is a complex compound which is formed by igniting a mixture of nitrogenous organic material, potassium carbonate, and scrap iron and extracting the mass with hot water. It forms large, yellow crystals, whence it is often called "yellow prussiate of potash."

In this compound the iron is bound to the carbon and nitrogen atoms, thus forming a negative radical. *A water solution of potassium ferrocyanide gives practically no iron ions.* It gives only potassium ions (K^+) and a complex tetravalent ion, which is called the ferrocyanide ion ($Fe(CN)_6^{----}$). When potassium ferrocyanide and a ferric salt are brought together, a deep blue precipitate, called **Prussian blue**, is formed. This compound is **ferric ferrocyanide**:

$$4\ FeCl_3 + 3\ K_4Fe(CN)_6 \longrightarrow Fe_4(Fe(CN)_6)_3\downarrow + 12\ KCl$$

Prussian blue is used as a pigment and sometimes for the preparation of laundry bluing. If the fabrics which are dipped into this bluing are not free from soap and alkali, ferric hydroxide may be formed on the cloth, producing spots of iron rust.

Ferricyanides. By treating a water solution of potassium ferrocyanide with chlorine, we get by evaporation garnet-red crystals of potassium ferricyanide ($K_3Fe(CN)_6$):

$$2\,K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\,KCl + 2\,K_3Fe(CN)_6$$

Potassium ferricyanide is called "red prussiate of potash" and in solution gives the trivalent ion $Fe(CN)_6^{---}$. The difference between the formulas for potassium ferrocyanide and ferricyanide can be remembered by noting that in each compound there are six (CN) groups which require enough metallic elements to make up a valence of six. In the *ferricyanide, iron is trivalent; in the ferrocyanide, divalent.*

Ferrous salts give with potassium ferricyanide a dark blue precipitate of ferrous ferricyanide (Turnbull's blue):

$$3\,FeCl_2 + 2\,K_3Fe(CN)_6 \longrightarrow 6\,KCl + Fe_3(Fe(CN)_6)_2$$

We can test for a ferrous ion by using potassium ferricyanide; and for a ferric compound by using potassium ferrocyanide; in both cases we obtain a blue precipitate. These two tests are frequently applied in distinguishing between ferrous and ferric salts. We do not obtain a dark blue precipitate with ferric salt and ferricyanide, or with ferrous salt and ferrocyanide.

446. Blue prints. The action of light will reduce the ferric salts of certain complex organic acids to ferrous salts. This reaction is taken advantage of in making **blue prints.** Paper can be treated with a ferric salt (ferric oxalate) in the dark and dried. It can then be exposed to light under a photographic negative or an ink drawing on tracing cloth. Where the light strikes the paper, the ferric compounds will be reduced to ferrous, and the amount of reduction will be in proportion to the amount of light that reaches the paper. After exposure the paper can be dipped into a solution of potassium ferricyanide, and wherever ferrous compounds have been produced, Turnbull's blue will be formed. Where the paper has been protected from the light,

there will be no action, and the unchanged ferric salt will be washed away. There is thus left a blue and white picture called a **blue print.**

Commercial blue-print paper is coated with a mixture of ammonium ferric citrate and potassium ferricyanide. The ammonium ferric citrate is the best ferric salt for the purpose. The developer, potassium ferricyanide, is put directly on the paper in the first place. After exposure to light such a paper is dipped into water, and the blue color is formed at once. It is then washed with water until all the unchanged chemicals have been removed; the print is now permanent.

447. Inks. An organic compound called **tannic acid** is obtained from certain vegetable products (*nutgalls*). With ferric salts this substance forms a jet-black, insoluble **ferric tannate.** A number of years ago a colloidal solution of this material in water was used as a **writing ink.** A better ink was later prepared by mixing a slightly acid solution of ferrous sulfate and tannic acid. *Ferrous tannate* is soluble and colorless, and no black color is produced until the mixture is exposed to air. To make the ink visible a blue dye is added; the writing slowly turns black as the ferrous salt is oxidized and ferric tannate is produced. This is the so-called **blue-black ink.** Ferric tannate is particularly suitable as a writing fluid because it is very permanent.

448. Ink spots and other stains. Ink spots which are fresh can generally be removed by simply washing with water, in which all the ingredients are soluble. After standing for some time, however, the ink spot contains the insoluble ferric tannate. Such a spot can be removed by treating it with a reducing agent which will reduce the ferric salts to ferrous. Ammonium oxalate or a dilute solution of oxalic acid is suitable for this purpose. Lemon juice contains an organic acid (citric acid) which is a reducing agent, and ink spots are often removed in the household by the use of lemon.

Rust stains are often rendered soluble by the same treatment as that used for ink spots. **Coffee** and **tea** stains can

be washed out of cotton or wool *by boiling water if it is applied at once.*

Stains on silk can seldom be entirely removed; hypochlorous acid (§ 297) should never be used on them.

Water will take out **sugar** and **sirup** stains. But for **grease** it is necessary to use some other solvent, such as carbon tetrachloride or gasoline, and to absorb the solution with blotting paper or clean white cloth to prevent its spreading.

Cobalt and Nickel

449. The properties and uses of the metals. These elements, like iron, form two series of salts in which the metals are divalent and trivalent respectively. Aside from their use in alloys, the elements are relatively of little importance. Both metals are, like iron, magnetic.

Nickel is a white, hard, malleable metal which can be highly polished. As this polish is not affected by moist air, a great many objects are plated with a thin coating of nickel, which gives them a pleasant appearance and prevents their corrosion. The nickel is plated on by means of an electric current.

Nickel is a component of a number of alloys. **Monel metal** contains approximately equal parts of copper and nickel; it is made by the smelting of a natural ore in which nickel and copper occur in these proportions. This alloy is used for modern rifle bullets, which are as hard as steel and much heavier. It is stronger than ordinary steel and has valuable acid-resisting properties. **Nickel steel,** containing about 5 per cent of nickel, is both hard and tough; hence armor plates for battleships are made of it. **Nickel for coinage** is made of three parts of copper and one of nickel. **German silver** contains copper, zinc, and nickel. All of these alloys find certain special uses because of their resistance to corrosion by moist air and chemicals.

Cobalt is a metal which closely resembles nickel. It is used for making a few special alloys. As there is no extensive commercial use for pure cobalt, the metal is not extracted on a large scale.

450. Typical compounds. The compounds of nickel and cobalt which are most extensively used are the cobaltous and nickelous compounds, such as cobaltous chloride ($CoCl_2$) and nickelous sulfate ($NiSO_4$). Nickel carbonyl ($Ni(CO)_4$) is a rather interesting and somewhat important substance: the **Mond process** for separating nickel from copper depends on the formation of nickel carbonyl and its sub-

sequent decomposition into pure nickel. It is a volatile, colorless liquid which is formed by passing carbon monoxide over warm, finely divided nickel. On heating to 180° C. it is decomposed into nickel and carbon monoxide.

SUMMARY OF CHAPTER XXXIV

IRON, NICKEL, AND COBALT are neighboring elements in the eighth group.

PURE IRON is not affected by cold water but when heated will decompose steam. It will burn in oxygen if heated sufficiently hot. Iron forms two series of compounds : the *ferrous,* in which iron is *divalent,* and the *ferric,* in which it is *trivalent.*

Ferrous compounds may be *oxidized* to ferric compounds, and the latter *reduced* to ferrous. *Oxidation* is a reaction which increases the valence of the positive element in a molecule; *reduction* decreases it.

Ferric hydroxide and ferrous hydroxide are insoluble substances. *Rust* is a mixture of ferric oxide and hydroxide. It is formed by the action of moist air on iron; it peels off and hence does not protect the iron.

IRON FORMS THE OXIDES FeO, Fe_2O_3, and Fe_3O_4. The latter can be formed as an adhering coating on iron by the action of steam. Such iron is called Russia iron.

Potassium ferrocyanide forms Prussian blue with a ferric salt. Prussian blue is used as a pigment and in making bluing.

Potassium ferricyanide gives a precipitate of Turnbull's blue with a ferrous salt. A ferrocyanide is a test for a ferric salt, and a ferricyanide for a ferrous salt.

BLUE PRINTS are made on paper coated with a reducible ferric salt and potassium ferricyanide. The ferric salt is reduced by light to ferrous. On being treated with water the potassium ferricyanide and ferrous salt combine, forming Turnbull's blue; the unchanged chemicals are washed away.

BLACK INKS are made from ferric tannate, a black, insoluble material. Blue-black inks contain ferrous tannate, which slowly oxidizes in the air to ferric tannate.

COBALT AND NICKEL are both magnetic, like iron. Metals are often coated with a film of nickel because it is not affected by air and because it takes a polish. Monel metal and German silver are alloys of nickel.

Questions and Problems

1. How does paint protect iron from rusting?

2. Compare the rusting of iron with the "rusting" of aluminum.

3. Why are the ferric compounds more stable than the ferrous?

4. Explain the fact that a solution of sodium carbonate precipitates the hydroxide and not the carbonate from a solution of a ferric salt.

5. Will ammonium hydroxide precipitate the iron hydroxide from a solution of any iron compound?

6. Write the equations for producing nascent hydrogen and using it to reduce ferric chloride.

7. What other oxidizing agents besides hydrogen peroxide might be used to change ferrous compounds to ferric?

8. How would you prove that a given solution contained *both* ferrous and ferric salts?

9. Why do the stains made by iron inks gradually become brown?

10. What properties have cobalt and nickel in common with iron?

11. Why is iron copper-plated before it is nickel-plated?

12. Name and give the uses for four nickel alloys.

13. What is the composition of Turnbull's blue? How is it prepared?

14. What precautions must be taken when Prussian blue is used for laundry purposes?

15. For what special purposes are blue prints adapted?

16. Find the percentage of iron in Prussian blue.

17. How many liters of chlorine (under standard conditions) will be needed to oxidize 1 kilogram of ferrous chloride?

18. How many cubic centimeters of dilute sulfuric acid (sp. gr. 1.09 and 13% H_2SO_4) will be required to dissolve 112 grams of pure iron?

19. Given 335 grams of ferric chloride, how many grams of sodium hydroxide will be required to precipitate all the iron as ferric hydroxide?

20. When the precipitate in problem 19 is heated to red heat, how much ferric oxide is left?

CHAPTER XXXV

ZINC, TIN, AND LEAD

Metallurgy in general — concentration — making the metal — zinc ores — zinc oxide and hydroxide — chloride — sulfide, its precipitation.

Metallurgy of tin — tin plate — stannous and stannic salts — recovery of tin from tin plate.

Metallurgy of lead — lead alloys — lead oxides — lead storage battery.

Replacement series of metals — electric cell — electrons in the cell — corrosion of iron.

451. The importance of metals. We have already met with two metals, aluminum and iron, which are prepared industrially in large quantities. These two elements together with copper, zinc, lead, and tin are the common metals, from which are manufactured tools, pipes, containers, building materials, elaborate machines, and the mechanical devices so important to our civilization. The question might be asked, if iron and steel are so cheap to manufacture, why are they not used for everything? Why are electric wires generally made of copper, water pipes of lead, and tin cans (in part) of tin? The answers to such questions are found in a consideration of the different properties of the various metals. In this chapter we shall consider these properties and discuss how zinc, lead, and tin are obtained from their ores.

452. Some general principles of metallurgy. A few metals, such as copper, silver, and gold, occur free in nature, and their manufacture into articles of commerce is, of course, comparatively simple. For the most part, however, the important

metals are found as compounds containing sulfur, oxygen, and silicon. Many compounds of the metals which occur naturally as minerals are not suitable for use in the preparation of the free metals. In general, *the oxides, sulfides, and carbonates,* when they are mined in a comparatively pure condition, *are the most suitable starting points.* Such substances are called **ores;** and the science that deals with the extraction of metals from their ores is called **metallurgy.**

453. Concentration. Hardly any ore is the pure compound which is desired. It is almost always contaminated with comparatively worthless rock (gangue). Some kind of sorting or concentration is needed before the product of the mine is ready for the chemical process of turning the compound into the element. The material is first crushed by mechanical mills and separated into coarse, medium, and fine portions by passing through sieves. The material is then ready for concentration. This may be done in some instances by hand picking, but more often is accomplished by gravity separation processes. In these processes the ore is agitated with water in such a manner that the heavy valuable material sinks and the bulk of the lighter gangue is washed away. In recent years the flotation process (see Chap. XXXVI) has become a very valuable method of concentrating many ores, particularly the sulfide ores of copper, zinc, and lead.

454. Making the metal. The methods of obtaining metals from their compounds may be classified as follows: (1) **electrolysis** of the fused salts, as in the preparation of sodium, calcium, aluminum; (2) **reduction** of the oxide or sulfide in a furnace. The expense of the electrical energy and the preparation of the pure compounds necessary for the electrolytic bath make the first method much more expensive than the second. Therefore, the electrolytic process is used only when the metal is so active (electropositive) that its oxide cannot be reduced with carbon. The metallurgy of iron is a good example of the general method

of obtaining metals from the oxide by reduction with carbon in a furnace. By heating the oxide of many metals with carbon or with carbon monoxide the free metal is obtained. When the ore is a sulfide, it is often first heated in the air (roasted) in order to convert it into the oxide.

If ores contained only the pure oxide or sulfide, metallurgy would be a much simpler art. But, as we saw in the case of iron, they are always more or less contaminated with other mineral material. This **gangue** usually consists of calcium or magnesium silicates, calcium carbonate, or free silica. The removal of the gangue is accomplished by using as a **flux** some material which will combine with it at a high temperature to form a fusible, glass-like material. The latter floats on the metal and is called **slag**. If the gangue is essentially an acid anhydride, like silicon dioxide, we add either lime or limestone; if the gangue is calcium carbonate (which goes into the oxide on heating), we add silica as a flux. In both cases *the slag is essentially calcium silicate.*

By bearing these general principles in mind we can more easily correlate and remember the metallurgy of the common metals.

Zinc

455. Metallurgy. The metallurgy of zinc is simple. The principal ores are the oxide called **zincite** (ZnO) and the sulfide called **zinc blende** (ZnS). The sulfide, on roasting, produces the oxide:

$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow$$

The oxide is mixed with finely powdered coal and heated in earthenware retorts (*R*, Fig. 239) in order to reduce it to zinc:

$$ZnO + C \longrightarrow Zn + CO\uparrow$$

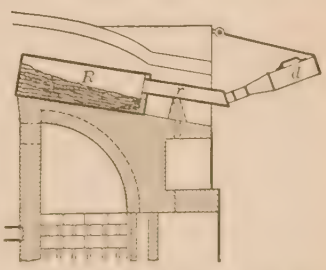


Fig. 239. Retorts where zinc oxide is reduced by carbon.

Since this metal boils at a temperature which can easily be attained (950°), it is separated from the impurities by *distillation*. The retorts are heated sufficiently hot (*r*), and the gaseous zinc passes into cold earthenware or iron receivers, where it condenses to a liquid. The molten metal is then run into molds and allowed to solidify.

456. Properties and uses. Zinc is a bluish white metal and, as it ordinarily comes from the smelter, is rather crystalline and brittle. At a temperature of about 100° C. it is malleable and ductile and can be rolled into sheets.

It is a constituent of a number of alloys, such as **brass** (copper and zinc), **German silver** (copper, nickel, and zinc), and **bronze** (copper, tin, and zinc). The metal has a limited application; it is used, for instance, as the negative plate of all electric batteries except storage batteries. **Galvanized iron** is iron covered with a thin layer of zinc. This is done by dipping the metal into molten zinc, or by a process of electroplating.

Compounds of Zinc

457. Zinc oxide and hydroxide. When zinc is heated sufficiently hot, it takes fire in the air, forming the *white oxide* (ZnO). The same oxide may be prepared by heating the hydroxide or zinc carbonate. Zinc oxide is used to make zinc ointment; also as a white pigment (**zinc white**) in the manufacture of paint; and very extensively as a filler in the manufacture of white rubber. **Zinc hydroxide** ($Zn(OH)_2$) is precipitated when sodium hydroxide is added to a zinc salt. Zinc hydroxide, like aluminum hydroxide, will dissolve in either acids or bases.

458. Zinc chloride. This salt ($ZnCl_2$) is obtained by dissolving zinc in hydrochloric acid. When it is evaporated it gives a white solid, which rapidly absorbs water from the air (deliquescent); for this reason it is sometimes used as a drying agent. Solutions of zinc chloride will dissolve oxides of many

metals and are therefore valuable for cleaning the surfaces of metals before soldering. Wooden posts and railroad ties which are impregnated with it are much more resistant to the action of decay and disintegration; hence considerable quantities of the salt are applied to this purpose.

Zinc sulfate ($ZnSO_4$) is another common salt of zinc, which is soluble in water; it forms transparent crystals ($ZnSO_4 \cdot 7\ H_2O$), which are called **white vitriol.**

Tin

459. Metallurgy. Tin oxide (SnO_2) is the only important ore of tin. The metal is produced by heating the oxide with carbon in a reverberatory furnace:

$$SnO_2 + C \longrightarrow Sn + CO_2 \uparrow$$

The molten metal which collects at the bottom of the furnace is drawn off and cast into ingots. These are afterwards remelted at a gentle heat, and the pure metal flows away from the impurities.

460. Tin plate. Tin is a white metal, soft and malleable. Pure tin is known ordinarily as **block tin.** It is very resistant to ordinary atmospheric corrosion and for this reason is widely used as the protective coating on other metals. Ordinary **tinware** (tin plate) is sheet iron or steel which has been coated with a thin layer of metallic tin by being dipped into the molten metal. This material is often erroneously called simply "tin."

Tin foil is tin hammered or rolled into thin sheets; most tin foil, however, contains considerable lead. Tin is used in making many alloys, which have already been considered.

Compounds of Tin

461. Stannous and stannic salts. Tin forms two series of compounds: one, called the stannous salts, in which tin has the valence of two, and the other, called the stannic salts, in which

the valence of tin is four. Stannous compounds have a very decided tendency to go over into stannic compounds and for this reason are strong reducing agents. For example, ferric chloride is reduced by stannous chloride:

$$\underset{\text{ferric chloride}}{2\,FeCl_3} + \underset{\text{stannous chloride}}{SnCl_2} \longrightarrow \underset{\text{ferrous chloride}}{2\,FeCl_2} + \underset{\text{stannic chloride}}{SnCl_4}$$

Lead

462. Metallurgy. The commonest ore of lead is **galena,** which is the sulfide (PbS). There are two methods of extracting lead from its ores: one is carried out in a reverberatory furnace, and the other involves the use of a blast furnace. The latter process is now most widely employed.

This blast furnace is much like an iron furnace, except that it is shorter and wider. The charge consists of ore which has first been roasted in an open-grate furnace. The roasting *partially* converts the ore into oxide. The other materials in the charge are coke and a flux consisting of a mixture of iron oxide and limestone; the gangue is usually quartz. The combustion of the coke furnishes the necessary heat, and the lead oxide is reduced by the carbon monoxide and the carbon; some iron is also formed by the reduction of the iron oxide. This iron in turn reacts with the lead sulfide, forming iron sulfide and lead:

$$PbS + Fe \longrightarrow FeS + Pb$$

Metallic lead and a slag form the two layers at the bottom of the furnace and are drawn off.

Lead ores usually contain gold and silver, which are found in the crude metal. As molten lead is an excellent solvent for these precious metals, materials which contain a small amount of them are chosen for the flux. In this way the process does two things at the same time: it produces lead and extracts the precious metals from very poor ores.

Lead obtained in this way contains a number of impurities, which make it hard. In order to get soft lead these must be removed. This is done by heating the metal in a reverberatory furnace at a low temperature. A scum, containing most of the

impurities, is formed and is skimmed off. Silver is removed by the Parke process, which we shall consider in the next chapter.

463. Properties, uses, and alloys. Lead is a soft, white metal with a brilliant luster when freshly cut. It is oxidized by the air, producing a thin adhering film, which protects it. Because it is easily cut and bent, and because its edges may be readily fused or soldered, lead is made into pipes and sheathing for cables. It can also be rolled into thin sheets and used as lining for tanks, electrolytic cells, and similar objects.

Lead is a low-melting metal and is a component of a number of low-melting alloys, such as **type metal** (lead, tin, and antimony), **solder** (lead and tin), and **lead shot** (containing either arsenic or antimony).

Compounds of Lead

The common compounds of lead are those in which the element is divalent and gives the ion Pb^{++}. Lead also forms a few compounds in which it is tetravalent; but these compounds are of less importance.

464. Lead oxides. **Litharge** (PbO), a yellow oxide of lead, is made by heating lead in air. It is very widely used in the preparation of paints and varnishes and in the manufacture of other lead compounds. A mixture of litharge and glycerol sets to a very hard mass and makes a valuable cement for laboratory purposes.

Another oxide of lead can be formed by heating metallic lead or litharge in the air at just the right temperature (about 400° C.). This is a red substance known as **red lead,** or **minium** (Pb_3O_4). It is put into paints as a pigment; it is also one of the substances which accelerate the drying of linseed oil. A paint made of it is very largely used on iron work, as it makes a satisfactory coating and is cheap.

Lead dioxide (PbO_2) is a brown powder made by treating red lead with nitric acid. It is a strong oxidizing agent.

465. Lead storage battery. The storage battery has come to be an essential part of the lighting and starting equipment of the automobile. It is also an important part of the reserve equipment of electric-power stations. *It is not an apparatus for storing up electricity which is to be drawn out at some future time,* but it is a device by which electrical energy is used to produce a chemical reaction; when this chemical action is reversed the cell delivers current. Thus the elec-

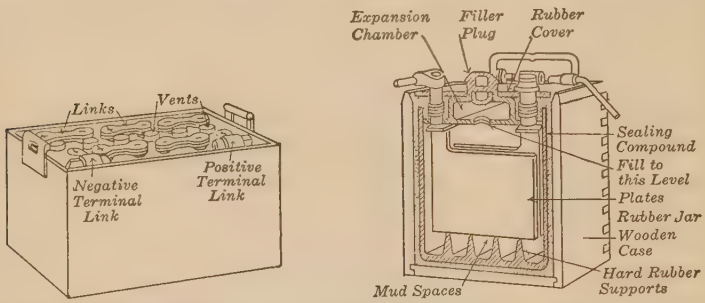


Fig. 240. Lead storage battery used on automobiles for starting and lighting.

trical energy is transformed into chemical energy in charging, and this in turn can be converted back again into electrical energy in discharging.

The usual automobile battery (Fig. 240) comprises either three cells (6 volts) or six (12 volts). Each cell contains lead plates dipping into dilute sulfuric acid. One set of plates, called the **negative** (−), is *gray* in color and contains pure, finely divided lead. The other set of plates, called the **positive** (+), is *dark brown* in color and is coated with lead dioxide (PbO_2). All the negative plates of one cell are joined to one another, and the positive plates are likewise connected. The two sets are sandwiched together with perforated insulators between. There is always one more negative plate than there are positive plates in each cell.

The reversible reaction which takes place in charging and discharging is as follows:

$$\text{Pb} + \text{PbO}_2 + 2\,\text{H}_2\text{SO}_4 \underset{\text{Charge}\longleftarrow}{\overset{\text{Discharge}\longrightarrow}{\rightleftharpoons}} 2\,\text{PbSO}_4 + 2\,\text{H}_2\text{O}$$

In discharging, the two plates come to the same condition ($PbSO_4$), and the acid is made more dilute by the formation of water. In practice the *cell is never allowed to become completely discharged.* In charging, the positive electrode (+) is attached to the positive terminal of a

direct-current generator, the plates are restored to their original condition, and the acid becomes more concentrated.

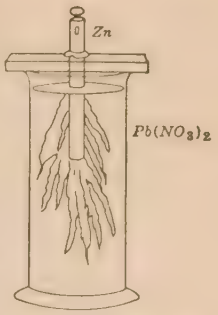


Fig. 241. Lead tree.

466. The replacement series of metals. We have already seen that metallic zinc can replace the hydrogen ion from an acid solution and set free hydrogen gas; and that in the case of the halogens there is a definite order in which one element can replace another from a solution. Such a series for the metals is shown below. For example, a strip of zinc placed in a solution containing the salt of any other metal below it in the series will form a zinc salt and precipitate the corresponding metal. Figure 241 shows zinc replacing lead in a solution of lead nitrate.

The reaction is as follows:

$$Zn + Pb(NO_3)_2 \longrightarrow Zn(NO_3)_2 + Pb\downarrow$$

or

$$Zn + Pb^{++} \longrightarrow Zn^{++} + Pb\downarrow$$

It should be noticed that hydrogen is given a place in the series because, like the metals, it forms a positive ion. Any metal above hydrogen can replace this element from an acid; for example, zinc and dilute sulfuric acid:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

or

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2\uparrow$$

Attacked by	Replacement Series of Metals
H_2O	Potassium
	Sodium
	Calcium
dil. acid	Magnesium
	Aluminum
	Zinc
	Iron
hot HCl	Tin
	Lead
	Hydrogen
HNO_3 or hot H_2SO_4	Copper
	Mercury
	Silver
$HNO_3 + HCl$	Platinum
	Gold

Elements below hydrogen do not liberate hydrogen when brought into contact with acids. The higher members of the series are so active that they decompose water. That is, they replace the hydrogen from water, which gives only a very minute concentration of hydrogen ions. The metals below aluminum have no appreciable action with hot or cold water and are therefore considered as *relatively inactive metals.*

467. The electric cell. We have already seen (§ 276) that when zinc dissolves in an acid, the electric positive charges are transferred from the hydrogen ions to the zinc atoms:

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$

If we place a strip of *pure* zinc and another of pure copper in a beaker of dilute sulfuric acid, we have a very simple electric cell. It will be remembered that *pure* zinc acts but very slowly on dilute acid; and hence only a slight action will be noticed between the zinc and the acid, and none at all with the copper. If, however, we connect these two strips of metal by a copper wire (Fig. 242), we shall see many bubbles of gas (hydrogen) coming from the copper. If we allow the action to continue for some time, we shall find that the zinc strip has visibly diminished and that the solution contains zinc ions. The copper is not changed, but considerable hydrogen has been liberated. If we connect a sensitive ammeter between the two strips, we find that a current is flowing from the copper (positive plate) through the wire to the zinc (negative plate). The ions of the electrolyte carry the electric current inside the cell from the zinc to the copper. Thus the chemical action between the zinc and the acid has been utilized to generate an electric current. *Any electric cell is a device for converting chemical energy directly into electrical energy.*

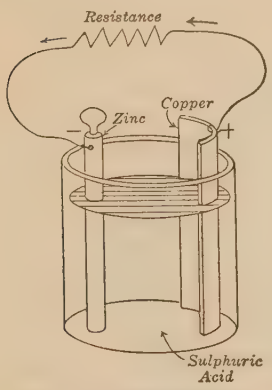


Fig. 242. Simple electric cell.

When any two metals in the replacement series are placed in a suitable electrolyte, they constitute a cell in which the

metal higher in the series is the negative pole and the lower one the positive. The farther apart any two metals stand in the series, the greater is the voltage produced by those two metals when used in a cell. For this reason the replacement series is sometimes called the **electromotive series.**

468. Electrons in the electric cell. When the zinc forms zinc ions, each atom of zinc loses two electrons:

$$Zn - 2e \longrightarrow Zn^{++}$$

These electrons have flowed through the copper wire from the zinc into the copper strip and have there supplied the necessary electrons to convert hydrogen ions into hydrogen atoms and molecules:

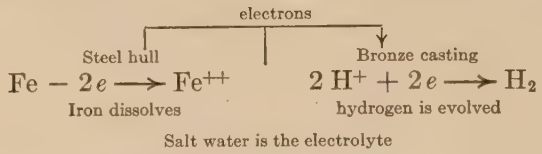
$$2H^{+} + 2e \longrightarrow 2H \longrightarrow H_2$$

In this way by making a complete circuit through which the electrons may travel and meet the hydrogen ion at another point in the solution, we have made zinc go into solution faster than it otherwise would. It must always be kept in mind that the flow of an electric current (as the term is used by electrical engineers) is in just the opposite direction to that of the electrons.

469. Corrosion of metals. We have found (§ 37) that the action of acid on zinc in a hydrogen generator is greatly hastened by adding copper sulfate. The reason for this is that a little copper is deposited on the zinc, which sets up a number of *small local electric cells.* For the same reason impure zinc and iron dissolve rapidly in acids, while the absolutely pure metals are attacked only very slowly.

The corrosion of metallic objects in contact with water or wet ground is largely electrochemical. When two different metals are in contact with each other in the presence of water, an electric cell is formed, and the more active metal corrodes. Thus, where the steel hull of a ship is in contact with a bronze casting (a mixture of copper and tin), special corrosion of the steel

practically always occurs, since iron is below copper in the replacement series.



Many similar cases of electrochemical corrosion occur if any metallic structure is in contact with water or wet soil. Even a piece of iron or steel by itself will often corrode in the same way because tiny electric cells are set up on the surface between the metal and the less active impurities. In our electrochemical cell solution was rapid, but with pure water the process is very slow, as only a few hydrogen ions are present. The presence of salts and oxygen accelerate the rate of corrosion. Salts act by increasing the conductivity (and in some cases the acidity by hydrolysis). The oxygen appears to act by reacting with the nascent hydrogen liberated on the less active metal, thus accelerating the action of the cell.

In addition to electrochemical corrosion, we must consider the the action of the oxygen of the air. This tends to form the oxide directly, and if the oxide has a different color from the metal, we say the metal " tarnishes." The process is hardly noticeable with zinc and aluminum, whose oxides are whitish like the metals, but is very striking with iron and in moist air with copper. Aluminum (Chap. XXXII) at once develops a thin oxidized skin, which is compact and adherent and prevents further oxidation. Tin, lead, and copper tarnish only slowly in normal air though the process may be much more rapid if excessive moisture or acid fumes are present. Tin keeps a bright appearance perhaps better than any of the other whitish common metals and is practically unaffected by moist oxygen.

470. The corrosion of iron. We can now apply what we have just learned to a consideration of an important industrial

problem; namely, the corrosion of iron. Absolutely pure iron is attacked only very slowly by dilute acids and therefore very slowly by the atmosphere. Impurities in it tend to set up tiny electric cells, which greatly hasten the solution of the iron. For this reason impure metals often corrode faster than very pure ones. *There are three general methods of preventing the corrosion of iron.*

In the *first* method we merely cover the iron with some sort of resisting paint which will adhere to it and as completely as possible shut out air, carbon dioxide, and water. A similar method substitutes for the paint a thin coating of some fusible silicate; various grades of enamel ware are made in this way.

The *second* method consists of coating the iron with an element like zinc (galvanized iron) which stands above it in the replacement series. At first sight it seems rather remarkable that a more active metal should be able to protect iron from corrosion. Since the zinc is more active than the iron, it goes into solution, and hydrogen comes out of solution on the iron surface, which is not attacked. As long as any zinc coating is left it will go into solution instead of the iron. In this way the iron is protected.

The *third* method of protecting iron involves coating it with some less active metal like tin (tin plate). In this case we depend on the inactivity of tin to prevent any corrosion at all; *this is satisfactory as long as the tin coating is perfect.* If corrosion starts, both the iron and the tin come into contact with slightly acid solutions, and the very worst possible conditions are at hand. Iron being more active than tin goes into solution, and hydrogen is deposited on the tin, which is not changed. Therefore, as soon as tin plate begins to corrode, it disintegrates more rapidly than pure iron.

SUMMARY OF CHAPTER XXXV

ZINC is made by reducing the oxide with carbon and distilling off the metal. It is a component of brass and bronze. It is used in electric batteries and for coating iron (galvanized iron).

Zinc oxide is used in making zinc ointment and as a paint pigment. *Zinc hydroxide* acts as a base with strong acids, and as an acid with strong bases. *Zinc chloride* is used to clean metals before soldering and as a wood preservative.

TIN is obtained by reducing the oxide with carbon. It is not corroded by the atmosphere and is used for coating iron.

It forms two sets of compounds: stannous (divalent) and stannic (tetravalent). *Stannous chloride* is made by the action of hydrochloric acid on tin. It is used as a reducing agent.

LEAD occurs chiefly as a sulfide. The ore is first roasted and then reduced in a blast furnace. It is used for piping, as a covering for cables, and in alloys, such as type metal, solder, and shot.

Lead forms the *oxides:* litharge, red lead, and lead dioxide. The first two are used in paints and the last is used in *storage batteries.*

IN THE REPLACEMENT SERIES OF METALS the position of any metal depends upon its relative tendency to ionize. Any element will replace any other element that stands below it.

IN THE CORROSION OF GALVANIZED IRON the more active metal zinc goes into solution; in the case of tin plate the iron goes into solution. *Tin protects iron* only as long as the entire surface is covered.

Questions and Problems

1. Why are there so many electrochemical works located at Niagara?

2. Name two reducing agents commonly used in metallurgy.

3. Explain the meaning of these terms: (*a*) *ore*, (*b*) *gangue*, (*c*) *flux*, (*d*) *slag*, and (*e*) *alloy*.

4. What advantages as a paint has zinc white over white lead?

5. What use has a tinsmith for a solution of zinc chloride?

6. Stannous chloride ($SnCl_2 \cdot 2\,H_2O$) gives an acid reaction with litmus paper. Give a possible explanation.

7. How would you test for the presence of zinc?

8. What are the disadvantages in using tin plate for covering roofs?

9. (*a*) How may lead be detected? (*b*) How would you test a sample of water for lead?

10. Give the formula and a use for each of the following: (*a*) *minium*, (*b*) *galena*, (*c*) *block tin*, (*d*) *litharge*, (*e*) *zinc blende*.

11. What advantages has lead for making water pipes? What disadvantages?

12. Why are pipes made of block tin commonly used in connections for soda-water fountains?

13. What is *galvanized iron?*

14. What changes take place in the plates of a storage battery when it is *discharged?* When it is *charged?*

15. What is the change in the density of the electrolyte in a lead storage battery during discharge?

16. What is the equation for the chemical change involved in charging a lead storage cell?

17. Summarize the facts you have learned from studying the replacement series of metals.

18. Explain why iron when coated with zinc is protected more effectively than when coated with tin.

19. What is the simplest formula of the compound which contains 22.7% of zinc, 11.1% of sulfur, 22.3% of oxygen, and 43.9% of water?

20. How much coke (carbon) would be needed for the reduction of one ton of tin oxide?

21. In the reduction of the tin ore in problem 20, how many cubic feet of carbon dioxide (under standard conditions) were obtained?

NOTE. By a coincidence, 1 ounce-molecular-weight of a gas has a volume of 22.4 cubic feet, and 1 pound-molecular-weight has a volume of 16 × 22.4 or 358 cubic feet. This is because

1 ounce = 28.3 grams

and 1 cu. ft. = 28.3 liters

TOPIC FOR FURTHER STUDY

The corrosion of iron and steel. What are some of the modern methods of preventing corrosion? Special iron alloys ("Duriron" and "Buflokast" iron, for example) are very resistant to corrosion. What do they contain besides iron? (Slosson's *Creative Chemistry.*)

Review Questions

1. Write equations for the following reactions, using formulas throughout:

(*a*) barium chloride and ferric sulfate
(*b*) ferrous sulfide and hydrochloric acid
(*c*) silver nitrate and hydrogen sulfide
(*d*) ferric chloride solution and metallic iron
(*e*) phosphoric acid and aluminum hydroxide

2. (*a*) Describe briefly a commercial method of producing metallic aluminum. (*b*) Explain the fact that aluminum retains its bright appearance in the air. (*c*) How is aluminum used to produce other metals from their oxides?

3. An experiment showed that 1.8 grams of magnesium displace from acid 1820 cubic centimeters of hydrogen, measured dry at 20° C. and 74 cm. (*a*) Find the volume of this gas under standard conditions, and (*b*) determine the valence of magnesium. (Atomic weights: Mg = 24.3, H = 1.008. 1 liter of hydrogen under standard conditions weighs 0.09 grams.)

4. Give the chemical formula and one use of each of the following: (*a*) carborundum, (*b*) red lead, (*c*) sand (pure), (*d*) quicklime, (*e*) plaster of Paris.

5. (*a*) What is meant by " hardness " in water? (*b*) Give a method for distinguishing between hard and soft waters. (*c*) Explain the cause of " permanent " hardness. (*d*) How can the latter be removed? (*e*) Give two important tests for impurities in drinking waters.

CHAPTER XXXVI

COPPER, MERCURY, AND SILVER

Metallurgy of copper — properties and uses — copper oxides and sulfate.

Mercury — mercurous and mercuric chloride.

Metallurgy of silver — silver nitrate — silver halides — photography — separation of metals into groups.

471. Action of acids on metals. It will be noted that the metals tin and lead come in the replacement series just *above* hydrogen. They dissolve in hot concentrated hydrochloric acid. In this chapter we shall study copper, mercury, and silver, which come just *below* hydrogen and can be dissolved only by nitric acid or hot sulfuric acid (oxidizing acids). In a following chapter we shall consider platinum and gold, the lowest members of this series of metals. These two are called the noble metals because they are attacked only by aqua regia (a mixture of nitric and hydrochloric acids).

Copper

472. Metallurgy. Free copper is found in large quantities in the Lake Superior region. In order to isolate **native copper**, it is necessary only to grind the rock to a powder and then to heat it until the metal runs together and flows to the bottom of the mass.

In Arizona copper is found as a basic carbonate called **malachite** ($Cu_2(OH)_2CO_3$), and in some places as the oxide **cuprite** (Cu_2O). The carbonate and oxide ores require only coal and heat to remove the oxygen.

Fig. 243. Mining copper with compressed air drills.

In Montana (Fig. 243) and Utah the copper occurs as sulfides, **copper pyrite** ($CuFeS_2$) and **chalcocite** (Cu_2S). The extraction of copper from the sulfide ores is difficult and often requires very complicated methods of treatment. The detailed metallurgy of these copper ores is too complicated for an elementary text.

473. Low-grade copper ores. It has recently been found possible and practicable to utilize ore containing even so small an amount of copper as only 2 per cent. By means of the **froth flotation process** about 85 to 90 per cent of the copper is recovered. The ore is first crushed to a fine powder and then mixed with water containing some cheap oil and sometimes a little sulfuric acid. This mixture is stirred vigorously and then allowed to flow into a large tank of water. Here the rock material at once settles to the

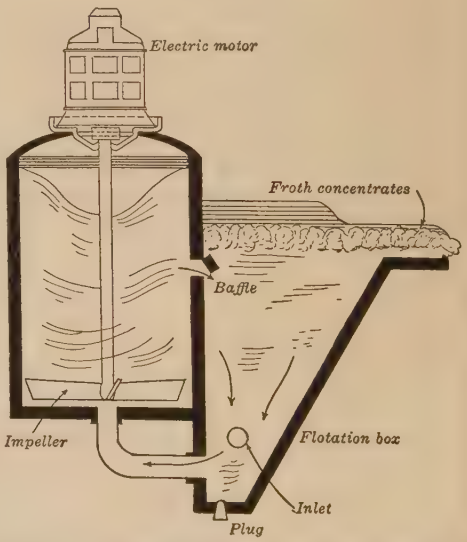


Fig. 244. Finely ground ore mixed with a little oil and acid are pumped in. The froth and ore are skimmed off.

bottom, while the bits of ore are held in the oily froth which rises to the top (Fig. 244).

474. Electrolytic refining. The copper obtained from the smelters always contains small amounts of other metals, including gold and silver. But even small amounts of impurities

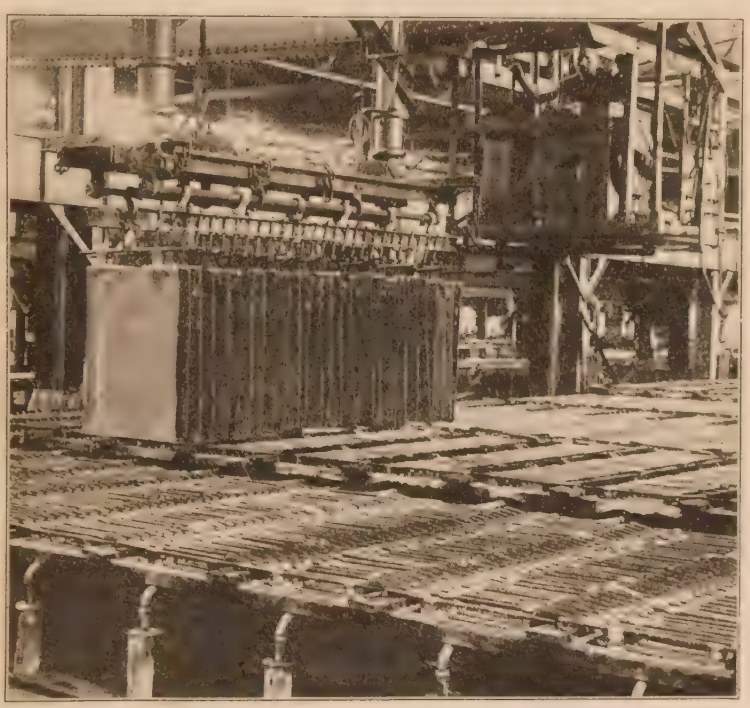


Fig. 245. Electrolytic refining of copper.

greatly impair the electrical conductivity of copper; therefore this metal must be further refined before being used.

This is done by a process of **electrolysis.** Thin strips of pure copper are made the cathode in a solution of copper sulfate ($CuSO_4$); thick plates of impure copper form the anode (Fig. 245). A current is passed through the cell, and elec-

trolysis takes place. The current is carried through the solution by the copper ions (Cu^{++}). Metallic copper is deposited at the cathode and dissolved at the anode. The copper thus obtained at the cathode is very pure (about 99.95 per cent); the impurities for the most part drop to the bottom of the tank and form what is known as the **anode slime.** The amount of gold and silver recovered from the slime is often sufficient to pay for this extra step in the refining of the copper.

475. Properties and uses. Copper is a malleable, ductile metal. It is the best conductor of electricity known, except silver. Copper is not affected by dry air but is slowly attacked under ordinary atmospheric conditions, forming a coating of a green basic carbonate. This coating is adherent and protects the metal from further action.

Copper in the form of wire, bars, etc., is very widely used as a conductor of electricity. Because of its resistance to corrosion, metal roofing for buildings and coverings for ships' bottoms are made of it.

Two widely used alloys of this metal are **brass,** an alloy of copper and zinc, and **bronze,** an alloy of copper and tin. **Phosphor bronze** contains in addition to these metals one to four per cent of phorphorus, which is present as the phosphide of one of the metals. It is a hard alloy not easily corroded, and is used for making such things as ships' propellers and shafting.

Compounds of Copper

476. Two series of copper compounds. Copper is like iron in that it forms two sets of compounds: the **cuprous** compounds, in which it is monovalent; and the **cupric** compounds, in which it is divalent. Most of the common compounds are cupric salts.

477. Oxides of copper. The most important cuprous compound is the red oxide of copper, **cuprous oxide** (Cu_2O), which is formed in testing for glucose by means of **Fehling's solution.** This solution contains copper sulfate ($CuSO_4$), potassium hydroxide, and Rochelle salt

($NaKC_4H_4O_6 \cdot 4\,H_2O$). When glucose is added to it and the mixture is boiled, cuprous oxide separates as a red precipitate.

Black oxide of copper, **cupric oxide** (CuO), can be made by heating copper in air and also by heating cupric hydroxide, nitrate, or carbonate:

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

478. Cupric sulfate, or blue vitriol ($CuSO_4 \cdot 5\,H_2O$). The hydrated sulfate of copper, or **bluestone,** is the most important of all the compounds of copper. It forms large, blue crystals. It is used in copper plating, and in electrotyping. A mixture

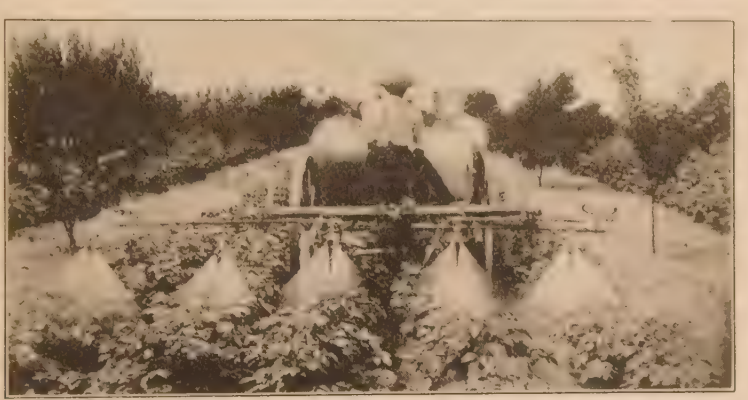


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Fig. 246. Spraying potato vines with Bordeaux mixture.

of copper sulfate and slaked lime, known as **Bordeaux mixture,** is employed as a fungicide to spray fruit trees, grapevines, and potato plants (Fig. 246). When the salt is added in minute quantities to water containing green scum, the plants (algæ) are killed.

Mercury

479. Occurrence and metallurgy. The principal ore of mercury is the sulfide (HgS), which is called **cinnabar.** The chief mines are in Spain and California.

Since mercury is volatile and not readily oxidized, it is easy to obtain the metal. The crushed ore is mixed with a little carbon and roasted in a current of air. The sulfur burns to sulfur dioxide, and the mercury vaporizes and is condensed:

$$HgS + O_2 \longrightarrow Hg\uparrow + SO_2\uparrow$$

The metal is redistilled to purify it.

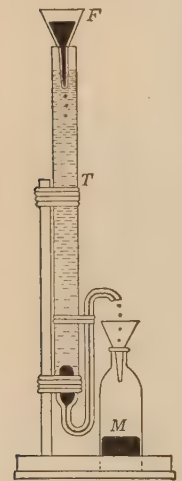

Fig. 247. Cleaning mercury by dropping through nitric acid.

480. Properties and uses. Mercury, or quicksilver, is a silver-white *liquid* which is 13.6 times as heavy as water.

We may pour some mercury into a glass tumbler and place an iron ball in the liquid. The iron (sp. gr. 7.9) floats.

It freezes at about $-39°$ C. and boils at 357° C. It forms alloys (called **amalgams**) with nearly all metals except iron and platinum.

On account of its high specific gravity the metal is used to fill barometers, and because it expands uniformly it is put into thermometers. For these purposes it must be free from other metals. Metals above it in the replacement series can be removed by the action of dilute nitric acid (Fig. 247).

Compounds of Mercury

481. Mercurous chloride, or calomel (HgCl). This is one of the three insoluble chlorides and therefore can be precipitated by adding a soluble chloride to a solution of mercurous nitrate:

$$NaCl + HgNO_3 \longrightarrow HgCl\downarrow + NaNO_3$$

It is a white solid which is commonly used in medicine to stimulate organs producing secretions.

482. Mercuric chloride, or corrosive sublimate ($HgCl_2$). Mercuric chloride is a white solid, soluble in water; it is a violent poison. It is made commercially by heating a mixture of common salt and mercuric sulfate. The sulfate is prepared by the action of concentrated sulfuric acid upon mercury. A very dilute solution of mercuric chloride, sometimes called the **bichloride of mercury,** is used as an antiseptic for sterilizing surgical instruments.

Silver

483. Metallurgy. Silver is very largely obtained through the **desilverization of lead** by **Parke's process.** Molten lead is treated with a small amount of zinc, whereupon an alloy of zinc and silver rises to the top and is skimmed off. This alloy also contains any gold which may be present. By heating it in a retort the zinc, which is a volatile metal, can be distilled off. The residue, containing lead, silver, and gold, is heated on a shallow dish in an open furnace. The lead is oxidized to the oxide, which melts and flows away, leaving a molten button of silver and gold behind.

The silver is separated from the gold by dissolving the button in hot, concentrated nitric acid. The silver goes into solution as silver nitrate, and the gold is unchanged. Metallic silver is thrown out from such a solution by plates of copper which are hung in it:

$$2\,AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,Ag\downarrow$$

The metallic copper goes into solution, replacing the silver.

484. Uses. Silver is primarily used in the making of coinage, jewelry, and ornaments, and in the plating of tableware. For coinage it is alloyed with about ten per cent of copper in order to make it more resistant to the wear and tear of common use. British coins contain 92.5 per cent silver; this is an alloy known as **sterling silver.**

485. Cleaning silver. Silverware tarnishes because of the formation of a black layer of silver sulfide (§ 176). This is usually removed by polishing with some slightly abrasive material. A recent method consists in boiling the silverware in an aluminum vessel containing a solution of sodium carbonate. The metallic aluminum in contact with the silver and the solution forms the negative pole of an electric cell; the silver serves as the positive pole. Aluminum goes into solution at the negative pole, and hydrogen is formed at the positive pole. This hydrogen reduces the silver sulfide to metallic silver. In this way all the silver sulfide is gradually converted into metallic silver, which is deposited on the original ware. The equations are:

$$Al - 3\,e \longrightarrow Al^{+++}$$

$$2\,H^{+} + 2\,e \longrightarrow 2\,[H]$$

$$2\,[H] + Ag_2S \longrightarrow 2\,Ag + H_2S$$

Compounds of Silver

486. Silver nitrate ($AgNO_3$). This compound is readily prepared by dissolving silver in nitric acid and evaporating the solution:

$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + NO\uparrow + 2\,H_2O$$

It melts easily without decomposition and may be cast into sticks (**lunar caustic**), which are sometimes used in surgery to burn away abnormal growths. It is the main source of other silver compounds.

487. Silver halides. We have already learned that when a soluble chloride is added to a solution of a silver salt, a white, curdy precipitate, **silver chloride** (AgCl), is formed:

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$$

In a similar way we may prepare **silver bromide** (AgBr) and **silver iodide** (AgI). These halogen salts of silver are all remarkable on account of their *sensitiveness to light*. The white silver chloride changes to a purple color on exposure to sunlight.

488. Chemistry of photography. We shall describe the production of a photograph in two steps: *first*, the preparation of the negative and *second*, the making of the print.

The glass plate or film which we buy is coated with gelatin and precipitated silver bromide (sometimes a little silver iodide also). This prepared plate is placed in a camera and exposed to the image which is produced by a lens properly focused on the object to be photo-

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A *B*

Fig. 248. Negative (*A*) and positive (*B*) of a picture of the late Charles W. Eliot.

graphed. If the plate is now examined, no visible effect seems to have been produced. But we can show by a further step, called developing, that the reduction of the silver bromide has been started on the exposed plate in exact proportion to the intensity of the light that fell upon each part.

To develop the latent image the exposed plate is put in a developer solution which contains a reducing agent such as pyrogallic acid or hydroquinone. The developer acts much more rapidly upon those portions of the plate where the illumination was most intense. The

reduced silver is deposited in the form of a black film. Thus the plate becomes darkest where the object was brightest, and vice versa; for this reason it is called a **negative** (Fig. 248 *A*). The unchanged silver bromide is now removed from the plate by putting it into a solution of sodium thiosulfate (hypo). This is called **fixing** the negative. It is finally washed and dried. The whole process which we have described must be carried on in a dark room or in a light-tight box, and must be carefully timed.

In **printing**, a sensitive paper is used which is coated with compounds that are very similar to those used on photographic plates. The negative is laid on the paper, and the latter is so exposed that the light must pass *through* the negative. In this way the light and dark are again reversed so that we once more get a positive (Fig. 248 *B*). The print is developed and fixed in the same manner as the plate. The print may be *toned* by dipping it into a solution of the salts of gold or platinum. The silver goes into solution, replacing these metals, and the gold or platinum takes its place. The gold gives to the photograph a reddish brown tone, while the platinum gives it a steel-gray tone.

489. Groups of metals for analysis. We have seen that the various metals form different insoluble compounds. For example, silver, lead, and mercurous salts form insoluble chlorides. A system of **qualitative analysis** of the metals has been devised which depends on the insolubility of certain salts. We can separate the metals into groups by the addition of reagents which will precipitate a salt of all the metals of a particular group. This is very convenient when we are analyzing a solution which may contain any one or all of the common metals. After we have separated the constituents of the solution into different groups, we then apply more special and complicated methods for detecting the presence in the group of any particular metal.

SUMMARY OF CHAPTER XXXVI

COPPER occurs as native copper, as the oxide, as the basic carbonate, and as sulfides. The oxide and carbonate are reduced with coal, but the sulfides require a difficult and complicated treatment.

LOW-GRADE COPPER ORES are now worked by the froth flotation process, in which the copper particles are floated away from the rock material by means of an oily foam.

ELECTROLYTIC COPPER is prepared by electrolysis, in which the anode is the impure copper plate, the electrolyte is copper sulfate solution, and the pure copper is deposited on the cathode.

USES OF COPPER — electric conductors, roofing for buildings, covering for ships' bottoms, and as one component in many alloys, such as brass and bronze.

COPPER SULFATE is the most important copper compound. It is used as a fungicide, for plating, and in some electric cells. Cuprous oxide is formed in testing for glucose with Fehling's solution.

MERCURY is obtained from the sulfide merely by roasting. It is a heavy liquid used in barometers and thermometers.

CALOMEL, mercurous chloride, is used in medicine. *Corrosive sublimate,* bichloride of mercury, is a deadly poison and is used in very dilute solutions as an antiseptic.

SILVER is largely obtained through the desilverization of lead by Parke's process. It is alloyed with copper for most purposes.

SILVER NITRATE is made by dissolving silver in nitric acid. It is used to make other silver compounds. The *silver halides* are insoluble compounds which are sensitive to light.

PHOTOGRAPHIC PLATES are coated with silver bromide, which after exposure to light can be reduced by a developer. The unreduced silver salt is dissolved by sodium thiosulfate. Prints are made on paper coated with silver halides.

ALL METALS MAY BE SEPARATED INTO GROUPS by taking advantage of the insolubility of certain compounds. This separation of the metals into groups by the addition of different reagents is the foundation of a system of *qualitative analysis.*

Questions and Problems

1. Write the formulas for the following ores: *copper pyrite*, *malachite*, and *cinnabar*.

2. Why is it difficult to extract copper from sulfide ores?

3. What is the principle involved in the *froth flotation process?*

4. What is meant by " electrolytic copper "?

5. Write the equation for the change which takes place when a strip of iron is placed in a solution of copper sulfate.

6. In order to nickel-plate a piece of iron it is first copper-plated. How would you copper-plate iron?

7. How would you prove that a given substance contained a compound of copper?

8. Why is mercury not used in the thermometers which are carried on Arctic explorations?

9. Show how the two chlorides of mercury illustrate the Law of Multiple Proportions.

10. What special precautions should be taken in regard to handling bichloride of mercury tablets?

11. What properties of silver make it useful for *coinage*, for *jewelry*, and for *tableware?*

12. What compound is formed when silver tarnishes?

13. How does sterling silver differ in composition and properties from pure silver?

14. A dime contains copper and silver. How could you prove the presence of each metal?

15. What is the function of " hypo " in photography?

16. What is the purpose of toning photographic prints?

17. Why must a negative be developed in a dark room with only a dim red light?

18. Compute the weight of water in 1 kilogram of blue vitriol.

19. How much copper goes into solution in order to replace 1 gram of silver from a solution of silver nitrate?

20. How many grams of silver nitrate could be prepared from a silver dollar which weighs 26.5 grams?

21. A certain copper ore has the formula $Cu_3(OH)_2(CO_3)_2$. Determine the percentage of copper.

22. How many pounds of mercury and how many cubic feet of sulfur dioxide (standard conditions) can be prepared from a ton (2000 lbs.) of cinnabar containing 90% HgS?

Topic for Further Study

Chemistry of photography. How is a photographic plate prepared? What change occurs during exposure? What developer is commonly used in developing tanks? Why? What precautions are necessary in fixing, washing, and drying? What is the chemistry of blue prints, silver prints, platinum prints, and the carbon process? (Louis Derr's *Photography for Students of Physics and Chemistry, Chemistry in Industry*, vol. 1; special pamphlets issued by the manufacturers of photographic supplies, such as the Eastman Kodak Company's *How to make Good Pictures*.)

CHAPTER XXXVII

DYES AND PAINTS

Color in its physical and chemical aspects.

Dyes — indigo and alizarine — mordants — lakes — coal-tar products.

Paints — water colors — shellacs and varnishes — oil paints — lacquers — pigments, white lead, lithopone, and other common pigments.

490. Historical development. The chemistry of colored substances is of great interest both practically and scientifically. Ever since the human race first developed a taste for pretty colors, a search for suitable dyes and paints has been in progress. At first man was limited to natural substances — inorganic and organic — and slowly developed an empirical art of applying these colors to pottery, cloth, stone, and wood. This art has been greatly modified and improved during the centuries. When man began to understand something about chemical compounds, he was able to devise better ways of making and applying the old colors. Finally, with the rapid development of chemistry in the last fifty years came the synthesis of a multitude of new dyes and pigments which have largely supplanted the earlier materials.

491. Concerning the physics of color. Experiments show that white light is composed of light of different wave lengths corresponding to the different colors in the spectrum. If a liquid allows one kind of visible light to pass through more readily than the other kinds, it appears colored to the eye. If white light falls on a very smooth surface, it may be reflected in

a beam, in which case we have a mirror; but with most surfaces there is diffuse (scattered) reflection. According to the physical and chemical nature of the surface, one or another of the wave lengths may be largely absorbed and not reflected; in this case the surface appears colored. If all the visible light is absorbed, the surface is black; if all is reflected to an equal degree, the material is white or gray. It is obvious that a surface may vary both in regard to the *amount* of diffuse light reflected and the *wave lengths* of the light. It is possible with the aid of a special spectroscope to measure these qualities of colors, and users of paints and dyes are now beginning to employ exact scientific terms in specifying their materials and products.

492. Chemistry of colors. Substances may reflect or transmit colored light either because of their physical condition or because of the inherent (chemical) nature of the molecules (or ions). The color of colloidal solutions is an example of what may be called physical color; ruby glass (colloidal gold) has already been mentioned. The blue or green color of many lakes is due to colloidal material, and the sky is believed to owe its color to colloidal material dispersed in the atmosphere. If the colloidal material causing these colors could be collected in a lump, it would be found to be of a very different color from that of the colloidal solution.

Attention has already been directed to the fact that the elements in the middle of the long periods of the periodic table often have colored ions and form colored compounds with colorless elements. We shall see in this chapter many illustrations of this generalization. The organic chemist has found that certain groupings of carbon atoms and nitrogen atoms give color to a compound; and this aspect of the science has been so far developed that it is possible to predict with considerable certainty the shade of a compound never before prepared. Thus the preparation of new organic colors (dyes) is no longer a "cut-and-try" process but proceeds along scientific lines.

Why do certain atoms and molecules absorb one sort of visible light while many others show no selective absorption? The answer to this scientific problem is left to the future; it may eventually be answered by the electronic theory of atomic structure. In the meantime, the chemists and physicists are adding new information to that already in existence and are able to formulate certain generalizations (such as those mentioned above) which tell us a great deal *about* colored compounds even if the fundamental cause of color still remains a mystery.

Dyes

The application of colors to fabrics is called **dyeing.** Dyes are colored substances which can be firmly attached to textiles

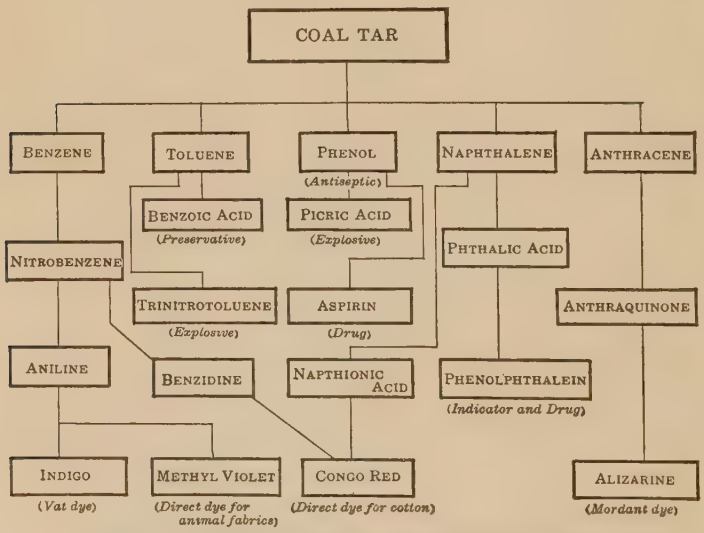

Fig. 249. Diagram to show some products from coal tar.

either directly or with the help of a colorless compound called a **mordant.** All the dyes now used are complex organic substances prepared from coal tar (Fig. 249). Their formulas are

far too complicated for consideration in any elementary course. Two of the most interesting are **alizarine** and **indigo**. For hundreds of years both these substances were obtained from plants; but in the last quarter of the nineteenth century chemists discovered how the molecules were constructed, and after much experimentation devised methods of preparing them from coal tar. The structure of indigo was established by Baeyer (Fig. 250), the most famous organic chemist of his time.

Fig. 250. Adolf von Baeyer (1835 1917). Famous German organic chemist; established structure of indigo.

493. Indigo is a dark-blue powder insoluble in nearly everything. It can be reduced to a soluble compound; and if cloth is impregnated with this reduced indigo and then exposed to air, the indigo is reformed by oxidation and dyes the cloth a very permanent blue. This illustrates one important method (called **vat dyeing**) of applying dyes (Fig. 251). Many new compounds of many different colors, similar to indigo in their dyeing properties, are now manufactured. These *vat dyes* are much used in dyeing *cotton*.

Many dyestuffs are soluble in water, and when the cloth is placed in such highly colored solutions, the dye becomes attached to the cloth. This is **direct dyeing**, and animal fabrics (silk and wool) are particularly easy to dye in this way. For example, a piece of wool or silk is dyed a light yellow by boiling in a solution of picric acid. It is thought that the combination

between the dye and the cloth is in many cases chemical, although the process of adsorption (§ 211) undoubtedly plays an important part.

494. Mordants. Many colored substances can be used as dyes only if employed in connection with a metallic hydroxide, called a mordant. **Alizarine** is such a **mordant dye.** It is a

Photograph by *Brown Brothers.*

Fig. 251. Dye house where piece goods are dyed.

yellow powder which when suspended in solution reacts with freshly precipitated hydroxides to form insoluble colored compounds. Such compounds are called **lakes** and are used in the manufacture of paints (§ 503).

If the hydroxide is precipitated on the cloth in the presence of the dye, it will bind the colored material to the fabric. A **mordant,** therefore, is a substance which will combine with a dye to form a colored compound and which is also held firmly by the fabric. In other words, *a mordant serves as an anchor between the dye and the cloth.* Aluminum hydroxide, iron hydroxide, stannous hydroxide, and stannic hydroxide are common mordants. The cloth is first treated with the salt of the metal, then with the dye, and finally steamed; the steam causes the hydrolysis of the salt, and the hydroxide is precipitated.

Because some dyes (*e.g.* alizarine) give different colors with different mordants, a pattern of colors may be dyed on a cloth in one dyeing. This is done by impregnating various parts of the cloth with different metallic salts according to the desired design. On boiling this cloth with the dye, the patterns appear in variegated colors, corresponding to the different mordants which were applied.

495. Tin chloride ($SnCl_4$). The metallic salts most used as mordants are those of aluminum, iron, and tin. The first two of these we have already considered (§ 461). **Stannic chloride**, the common salt of tin, is prepared in large quantities in the removing of tin from tin plate by the action of chlorine:

$$Sn + 2\ Cl_2 \longrightarrow SnCl_4$$

It is a colorless liquid fuming in air and forming crystalline hydrates with water, in which form it is usually sold.

Stannic hydroxide ($Sn(OH)_4$) is precipitated when sodium hydroxide is added to a solution of stannic chloride:

$$SnCl_4 + 4\ NaOH \longrightarrow Sn(OH_4) \downarrow + 4\ NaCl$$

This hydroxide has properties more definitely acidic than basic and is therefore sometimes called **stannic acid.** It readily dissolves in an excess of sodium hydroxide, forming sodium stannate:

$$Sn(OH)_4 + 2\ NaOH \longrightarrow Na_2SnO_3 + 3\ H_2O$$

Stannic acid in the form of its salts is extensively used in the preparation of silk goods. Silk cloth is treated with a solution of a tin salt and then with sodium hydroxide. The cloth becomes impregnated with stannic hydroxide, which is distributed through the finished fiber in some sort of solid colloidal solution and gives to the goods the desired weight and finish. Cotton goods are rendered noninflammable by a similar treatment. The amount of stannic acid which both cotton and silk can take

up and hold is very surprising. Silk often contains as much as twice its own weight of metallic tin in the form of stannic acid.

Certain dyes containing basic groups are direct dyes for wool and silk but not for cotton. They may be applied to this fabric by first impregnating it with tannic acid (a natural product), which acts as a mordant for these dyes.

In a warm 1 per cent solution of malachite green or magenta, strips of the following fabrics are placed: wool, silk, and cotton (previously soaked in 5 per cent tannic acid). After a few minutes they are removed and thoroughly washed with soap and water. All except the unmordanted cotton will have been dyed.

496. Coal-tar products. A tarry material obtained as a by-product from the manufacture of coke (Fig. 252) contains small amounts of certain hydrocarbons, called **aromatic compounds.** These hydrocarbons may be separated from the tar by distillation. From them can be made a whole host of substances of great value, including *all the dyes now in use.* Medicinal products (drugs), photographic developers, and explosives (*e.g.* picric acid) are also made from the aromatic hydrocarbons. Drugs and dyes are often called "coal-tar products"; but it must not be thought that the drug or color is present in the tar and need only be extracted by some process. Coal-tar products are made by starting with an aromatic hydrocarbon (from coal tar) and preparing carefully step by step a whole series of compounds, until finally one is formed which is the required dye or drug. A list of the important coal-tar hydrocarbons is as follows: benzene (C_6H_6), toluene ($C_6H_5CH_3$), and xylene ($C_6H_4(CH_3)_2$), which are

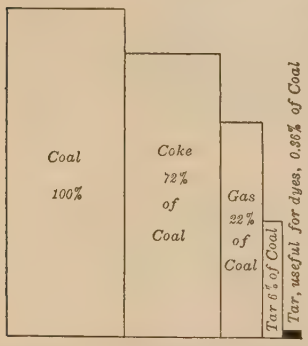

Fig. 252. Diagram to show amounts of by-products obtained in the distillation of coal.

liquids often used as solvents; naphthalene ($C_{10}H_8$) (a solid commonly sold as "moth balls"), and anthracene ($C_{12}H_{10}$), which is also a solid.

Paints

497. Two components. Dyes are primarily used to make cloth more attractive and pleasing to the eye. Paint is used both for decorative purposes and as a protection against corrosion or decay. A paint is composed of a **vehicle** (or medium) and a **pigment.** The vehicle is some liquid which more or less rapidly changes to a flexible, transparent, hornlike material when exposed to the air in thin layers. This change may be the result of oxidation or of evaporation of one of the constituents of the liquid. Oil paints "dry" because of oxidation; water colors, pyroxylin paints (lacquers), and spirit varnishes (shellac) dry by evaporation of one of the components.

In **water colors** the vehicle is glue and water; the latter evaporates leaving the pigment imbedded in a layer of solid glue. Certain water paints are made with a glue which on exposure to air slowly becomes insoluble. Such water paints are resistant to subsequent action of water.

Shellacs and **varnishes** are made from natural gums and synthetic resins; no pigment is used. The finest varnishes are made from fossil gums heated with oils. They dry largely by oxidation. Shellac is a gum produced by multitudes of insects on certain trees in the tropics. It dissolves in alcohol, and the solution dries by evaporation leaving a coating of shellac. **Spirit varnishes** are similar solutions of other gums in various solvents.

498. Oil paints. Certain vegetable oils which are esters of highly unsaturated organic acids (Chapter XXX) absorb oxygen. This process of oxidation results in the formation of a very tough, impervious, but transparent substance. It takes place when a layer of oil painted on a surface is left for a few days. These oils are called **drying oils** (though the process is

really *not* drying). **Linseed oil** is the most important. **Dryers,** which are substances like lead, manganese, and cobalt soaps, are added to oil paints to accelerate the oxidation of the oil; their action is catalytic. The **pigment** of the paint is some substance which will reflect much light (highly opaque), and is usually a white substance, such as white lead. A colored pigment is added if a colored paint is desired. Oil paints are often thinned with **turpentine** (from the sap of certain pine trees) because it hastens the drying of the paint, both by its catalytic action and by evaporation.

499. Lacquers (pyroxylin paints). This name is applied to those rapidly drying paints which have been developed since the

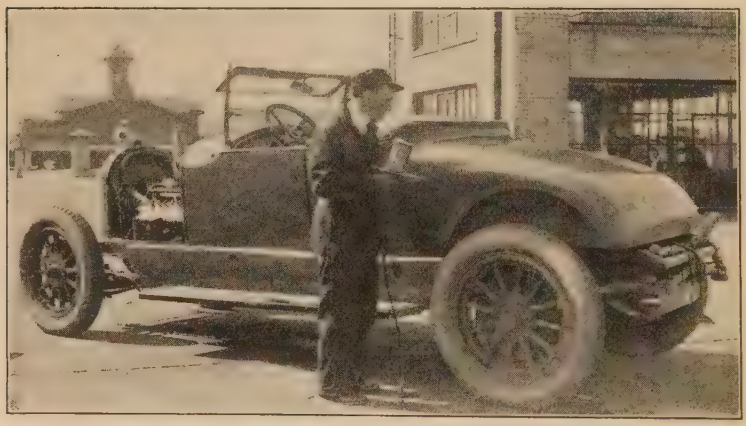

Fig. 253. Using compressed air to spray paint on an automobile.

war for use in the automobile industry. Much the same pigments are employed as in oil paints; but the vehicle is a solution of **pyroxylin** (soluble nitrocellulose) (§ 381), and certain very high-boiling organic liquids (plasticizers) in organic solvents. The solvent evaporates and leaves the pyroxylin and plasticizer as a tenacious and impervious coating. Such paints *dry by evaporation,* and the process is very rapid. Because of the nature

of the vehicle, pyroxylin lacquers are often applied by spraying (Fig. 253) or dipping. This is much cheaper and more rapid than applying the paint with a brush. The lacquers are now widely used in the automobile and furniture industries. **Gold** and **silver** lacquers are suspensions of bronze powder or aluminum powder in pyroxylin solutions.

Many solvents are used in this newly developed industry. Among them may be mentioned organic esters: ethyl acetate (§ 382) and the acetate of the butyl alcohol, which is made by special fermentation of corn. Such a combination of solvents and plasticizers must be used that evaporation takes place rapidly, but not too rapidly, and a coat of pyroxylin is left which will not shrink.

500. Pigments. The white pigments give body to both oil paints and lacquers, and on them depends what is known as the hiding power of the paint. **White lead** is the oldest and is still much used. **Lithopone** is a relatively new product that has gained wide use. **Zinc oxide,** or zinc white (ZnO), is another important white pigment. Barium sulfate (barytes), calcium carbonate (whiting), and calcium sulfate (gypsum) are often mixed with the other white pigments; they are called **extenders** since they serve to dilute the opaque pigment, having themselves but little hiding power.

501. White lead ($Pb(OH)_2 \cdot 2\,PbCO_3$). This substance is essentially a mixture of lead hydroxide and lead carbonate (called a basic carbonate). It is a heavy, white, insoluble substance. The disadvantage in using white lead is that it turns black when it comes in contact with hydrogen sulfide, because of the formation of black **lead sulfide** (PbS). Hydrogen sulfide is always present in small amounts in city air, and for this reason white paint often turns dark. Zinc oxide and lithopone are superior to white lead in this respect. White pigments containing zinc will not darken because zinc sulfide itself is white.

White lead can be manufactured by a number of different processes, all of which depend on the action of water, air, and carbon dioxide on

metallic lead in the presence of a weak acid like acetic acid. The old Dutch process, which is still used, gives an excellent product. Gratings of lead, called "buckles," are put in pots, as shown in figure 254. In the bottom of the pots is placed dilute acetic acid (vinegar). They are then buried in a mass of moist tanbark or manure (Fig. 255). The decomposition of the organic material in the manure or bark produces carbon dioxide and moisture; heat is also given off. The vapors of the dilute acetic acid attack the warm lead, forming lead acetate. The carbon dioxide and water react with this and produce white lead. After three or four months the lead is completely corroded, and in its place is a mass of white lead. The pigment is now separated from any unchanged lead (Fig. 256), is ground, and passed through sieves. It is finally ground in linseed oil and is sold as a thick paste. Several newer processes are now used for carrying out the same reaction in a shorter time.

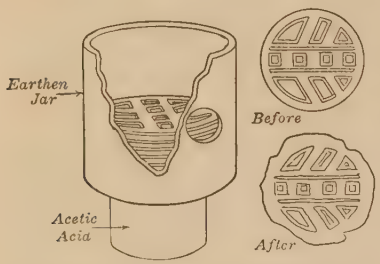

Fig. 254. White-lead buckles and earthen pot.

502. Lithopone. A mixture of barium sulfate and zinc sulfide (lithopone) is prepared by the action of barium sulfide on zinc sulfate:

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

It is extensively used as a flat wall paint because it has great hiding power, is not poisonous, and does not darken in the presence of hydrogen sulfide.

503. Colored pigments. Originally colored minerals were the sole pigments that were available, and many of these are still used, especially for the expensive oil and water paints used by artists. The list has been greatly supplemented by the inclusion of **lakes** (§ 494) made from a variety of synthetic organic dyes, and by colored compounds prepared industrially. The elements chromium, iron, and copper, which are in the middle of the first long period of the periodic table (page 305), are relatively abundant in the form of compounds and yield

Fig. 255. Filling pots with metallic lead buckles.

Fig. 256. Emptying pots of white lead corroded by the Dutch process in a stack. The large tube is the dust collector.

many valuable pigments. Compounds of lead and mercury (in the second long period) are also employed, although compounds of the latter element are too expensive for ordinary paints. Lampblack or carbonblack is the basis of almost all black paints. Some of the more common pigments are listed in the table; it will be noted that many are oxides.

Some Common Pigments

Shade	Name	Formula
Black	Lampblack or carbonblack	
Blue	Prussian blue	$Fe_4[Fe(CN)_6]_3$
Blue	Ultramarine	
Green	Mixtures of chrome yellow and Prussian blue	
Green	Copper aceto-arsenate	
Yellow	Lead chromate (chrome yellow)	$PbCrO_4$
Yellow-brown	Yellow ochre, sienna, from minerals containing hydrated iron oxide	
Red	Vermilion	HgS
Red	Venetian red	Fe_2O_3
Red	Red lead made by heating litharge to 400° (used particularly as a protective coating for iron)	Pb_3O_4
Red	Insoluble red organic compounds related to coal-tar dyes and lakes of *aluminum* and organic dyes.	

Ultramarine is made by fusing together aluminum silicate, sodium carbonate, sodium sulfate, sulfur, and charcoal. The blue color is probably due to a colloidal suspension of sulfur in the solid. It appears to be identical with the expensive mineral lapis lazuli.

504. Other uses of pigments. Many pigments are used in the preparation of colored printing inks. These are suspensions of the pigment in linseed oil, which has been heated to the boiling point until it is a sticky, thick mass. Black printing ink is a suspension of lampblack in this medium and turpentine.

Pottery is colored by means of inorganic pigments which are not changed by extreme heat. The method of application has been discussed in Chapter XXXII.

SUMMARY OF CHAPTER XXXVII

COLOR of an object depends on the wave lengths of light reaching the eye. Substances may reflect or transmit colored light.

Some colors are due to the physical condition of the material, and others to the chemical nature of the molecules or ions.

NEARLY ALL DYES now used are prepared from coal tar.

DYES may be classified as:

(1) *direct* dyes, which combine directly with the fiber, such as picric acid with animal fibers;

(2) *mordant* dyes, such as alizarine, which require an intermediate substance (metallic hydroxide) to fix the color on the fiber;

(3) *dyes which are formed by oxidation in the fiber* (vat dyes), such as indigo.

A PAINT consists essentially of *three* parts:

(1) a *pigment,* a finely divided, insoluble, colored powder;

(2) a *vehicle,* a liquid carrier for the pigment, which oxidizes in the air to form a hard, elastic surface;

(3) a *dryer,* a substance which hastens the drying process.

LACQUERS are pyroxylin paints. These rapid-drying paints use as the vehicle a *pyroxylin solution,* which consists of certain lower nitrates of cellulose and very high-boiling organic liquids dissolved in organic solvents.

QUESTIONS

1. What important change has taken place in the last fifty years in the methods of manufacturing dyes and paints?

2. What is the physical difference between a black card and a white card?

3. Why does a blue coat sometimes appear black when seen in artificial light?

4. Fabrics are often classified as *animal* and *vegetable*. Classify the following: (*a*) silk, (*b*) linen, (*c*) rayon, (*d*) flannel, (*e*) burlap.

5. What is a mordant? Name four mordants and write the formula for each.

6. Explain how the same dyestuff may be used to produce different colors.

7. What advantages have oil paints compared with pyroxylin paints?

8. Why have lacquers become so popular in the automobile industry?

9. Name five points which should be considered in judging of the value of a paint.

10. What is the function of the turpentine which is often added to an oil paint?

11. What is the distinction between paints and varnishes?

12. (*a*) Name five characteristics of a good varnish.
(*b*) How would you test a varnish?

13. Why would you not use white lead in a chemical laboratory?

14. Name and give the formulas for *three* pigments which contain lead.

15. What do the terms " fast " and " fugitive " mean as applied to dyestuffs?

Topics for Further Study

The story of indigo. Where is natural indigo produced? How was it prepared from the plant? Is synthetic indigo the same chemically as natural indigo? What is the starting point for synthetic indigo? What determines its price? (Slosson's *Creative Chemistry;* consult the *Encyclopedia Britannica.*)

Practical tests for paints and varnishes. Try out some methods for practical testing suggested in Bulletin No. 69 on *Paints and Varnishes*, U. S. Bureau of Standards. Then mount some illustrative samples on heavy cardboard and prepare descriptive legends. This might serve as a poster for Practical Chemistry.

Influence of coal tar on civilization. Prepare a chart showing some important dyes, drugs, photographic developers, explosives, perfumes, and flavors which are prepared from coal tar. Indicate on the charts the more important steps in their preparation. (*Chemistry in Industry*, vols. 1 and 2; Caldwell and Slosson's *Science Remaking the World*, and Slosson's *Creative Chemistry.*)

CHAPTER XXXVIII

LESS COMMON METALS AND THEIR USES

Gold — occurrence and extraction — properties — uses. Platinum — properties — uses. Manganese — manganese dioxide — permanganates. Chromium — oxides and hydroxides — chromates and dichromates. Tungsten, molybdenum, vanadium.

In this chapter we shall discuss two rare metals which are of great value, gold and platinum. We shall also briefly consider a number of metals which are not very common, but which have one or two important compounds or important uses.

Gold

505. Mining and extraction. Gold is found almost entirely in the free state and is often distributed through quartz or sand. The process of extraction involves its separation from the great mass of surrounding material. This may be done in some cases by merely taking advantage of the fact that gold is much heavier than the other mineral matter about it. When it occurs in alluvial deposits, the gravel may be washed in shallow pans in such a way that the sand, which is light, is carried away by the water and the heavy metal sinks to the bottom and is caught. In **placer mining** the ore is carried down a long trough in a stream of water; the gold settles to the bottom, where it is caught on cleats which are nailed to the floor of the trough. Another method of working the deposits involves crushing the ore in stamp mills (Fig. 257) and passing the crushed ore over copper plates coated with mercury. The mercury readily dissolves the gold, forming an amalgam. This amalgam is

scraped from the copper plates and the mercury distilled away from the gold. Still another method, called the **cyanide process,** is used to extract the gold left in the tailings. Metallic gold is soluble in sodium cyanide (NaCN) solution in the presence of air and forms a compound, sodium aurocyanide ($NaAu(CN)_2$). The gold can be displaced from this solution by metallic zinc, or deposited by electrolysis.

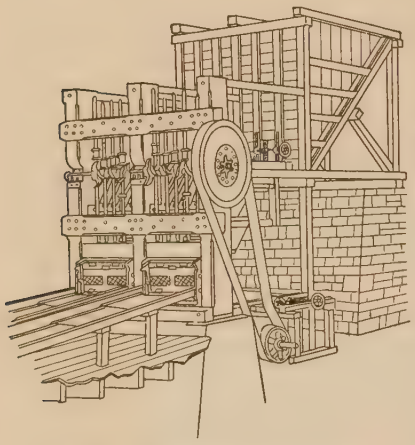

Fig. 257. Stamping mill for gold.

506. Properties. Gold is a very heavy metal (density 19.3 g./cc.) with a yellow color. It is the most malleable and ductile of metals and is a good conductor of electricity. It melts at about 1100° C. It is so soft that it is usually alloyed with copper in making gold coins and other gold objects. Pure gold is "24 carat" fine; gold used for jewelry is usually 18 carats.

Gold is a very inactive metal and is not affected by moisture, oxygen, or the common acids. It combines directly with the halogens, and for this reason is soluble in aqua regia (hydrochloric and nitric acids mixed). **Gold chloride** ($AuCl_3$) can be prepared by the action of gold and chlorine. This substance readily dissolves in hydrochloric acid, forming **chlorauric acid** ($HAuCl_4$). This is the substance which is formed when gold is dissolved in aqua regia. The acid dissociates to give the ions H^+ and $AuCl_4^-$.

507. Uses. Gold finds its principal use as the standard of currency and exchange in almost all civilized countries. It can be beaten out into thin leaves (gold leaf) which are only

$\frac{1}{250,000}$ of an inch thick, and applied as a coating. The potassium salt of chlorauric acid ($KAuCl_4$) is used in toning photographs. By the use of a gold anode it can be electroplated on silver or other metals from a bath of the double cyanide of sodium and gold.

Platinum

Platinum is found in the free state in alluvial sands, chiefly in the streams of the Ural Mountains. Its separation from osmium and iridium, two other metals which occur with it, is a complicated process.

508. Properties. Platinum is a whitish metal which is malleable and ductile. It melts at a fairly high temperature (1800° C.) but not in the Bunsen flame. It is affected by very few reagents but will dissolve in aqua regia, forming, like gold, a complex acid. This is called **chloroplatinic acid** (H_2PtCl_6).

When the ammonium salt of chloroplatinic acid is ignited, it leaves a porous mass of platinum, known as **platinum sponge.** This sponge may be distributed over the surface of asbestos if the asbestos is dipped in chloroplatinic acid and heated. Such a material is called **platinized asbestos.** Both platinum sponge and platinized asbestos are very powerful catalysts for gaseous reactions. **Platinum black** is platinum powder made by the action of a reducing agent on a solution of platinum salts. Platinum black is also a good catalyst and is often used either dry or suspended in a liquid.

509. Uses. Since platinum melts at a very high temperature and is not attacked by most chemicals, it is a useful material in the laboratory in the form of wire and crucibles (Fig. 258). Because it has the same coefficient of expansion as glass, it was formerly the substance selected when it was necessary to seal a wire into a glass vessel. If copper wire is taken in its stead,

the glass invariably breaks because copper and glass contract at different rates on cooling. This use of platinum has now been superseded by **platinite** (§ 438). Since the metal is not oxidized by the air even when heated, it has been used in electrical apparatus for contact points; but now **tungsten** is

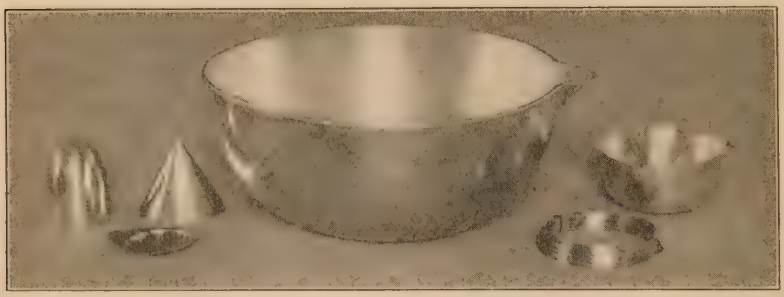

Fig. 258. Platinum wire and dishes used in the laboratory.

taking its place, being harder and cheaper. Platinum is used in place of gold in the manufacture of rings and other jewelry. It is at present much more valuable than gold.

Manganese

Manganese is peculiar in that it can form many oxides. That is, it can form a number of compounds, in each of which it has a different valence. In some of these it acts like a metal and forms a positive ion, and in others it is a constituent of the negative ion. Because of this multiplicity of compounds we shall not attempt to discuss the element fully.

The **manganous salts,** in which the element has the valence of two, are pink in color; they correspond somewhat to ferrous salts. The other compounds of manganese that are important are those containing oxygen.

510. Manganese dioxide. This substance occurs in nature and is known as **pyrolusite** (MnO_2). It is a strong oxidizing

agent. We have already employed it in the preparation of chlorine from hydrochloric acid:

$$MnO_2 + 4\ HCl \longrightarrow MnCl_2 + 2\ H_2O + Cl_2\uparrow$$

It will be noticed that the valence of manganese has changed from 4 to 2 in this reaction. Manganese dioxide is also used in the preparation of dry batteries, and as an oxidizing agent in black paint.

Metallic manganese and its alloy with iron (ferro-manganese) can be made from pyrolusite by reduction with aluminum (Goldschmidt process). The metal finds certain uses in the preparation of special steels.

511. Permanganates. When manganese dioxide is heated with potassium hydroxide and an oxidizing agent (like potassium nitrate), a green melt is obtained. On extracting this with water we obtain a solution of **potassium manganate** (K_2MnO_4). The green solution on being diluted with water changes to a purple color, and manganese dioxide is precipitated. By evaporating the purple-red liquid, we obtain needle-shaped crystals of **potassium permanganate** ($KMnO_4$). This salt in solution gives the ions K^+ and MnO_4^-. It is a very strong oxidizing agent, readily giving up oxygen to other materials and forming manganese dioxide or a manganous salt. It is used in the laboratory as an active oxidizing agent and in medicinal work as an antiseptic and disinfectant.

Chromium

Chromium is a metal occurring in group VI and in the middle of a long period. Like manganese it forms salts in which it has a number of different valences. In its higher valence it is a constituent of the negative ion of oxidizing acids.

512. Oxides and hydroxides. There are two important oxides of chromium, the green oxide, **chromic oxide** (Cr_2O_3),

and the red oxide, **chromic anhydride** (CrO_3). The former is the anhydride of a base, chromium hydroxide ($Cr(OH)_3$). From this base can be prepared various salts known as **chromic salts,** of which the sulfate ($Cr_2(SO_4)_3$) is important. Chromic hydroxide ($Cr(OH)_3$) is prepared by precipitation from the sulfate and is used as a mordant in dyeing.

Metallic chromium may be obtained from chromic oxide, which occurs naturally, by reduction with aluminum (Goldschmidt process). The metal is used in the preparation of special steels.

513. Chromates and dichromates. Chromic anhydride (CrO_3) readily dissolves in water, forming **chromic acid** (H_2CrO_4). The salts of this acid are called **chromates. Potassium chromate** (K_2CrO_4) is a yellow, crystalline solid, soluble in water. **Lead chromate** is an insoluble precipitate which, as we have already seen, is a yellow pigment.

Potassium dichromate ($K_2Cr_2O_7$) is formed when we evaporate a solution of potassium chromate in the presence of sulfuric acid:

$$2\,K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

The dichromate differs from the chromate by only a molecule of chromic anhydride ($K_2CrO_4 \cdot CrO_3$). In water solution it again forms the chromate ions. It is used in the tanning of leather.

Chromates and dichromates are both strong oxidizing agents in acid solutions; they are reduced to chromic salts. They are employed as oxidizing agents in the laboratory and to some extent in the industries. Potassium dichromate is used in **tanning light leathers,** since in the presence of a reducing agent chromic hydroxide ($Cr(OH)_3$) is precipitated in the leather. A solution of chromic anhydride in concentrated sulfuric acid is essentially a mixture of chromic and sulfuric acids. This is often used as a **cleaning solution** in the laboratory because it will readily dissolve greases and other material.

Tungsten, Molybdenum, and Vanadium

These three elements, like chromium and manganese, form a multitude of compounds in which they have a number of different valences and have either acidic or basic properties. The chief use of the metals lies in the preparation of special steels. The pure metals themselves are rarely manufactured; but their alloys, called **ferro-alloys,** containing about 50 per cent of iron, find important uses. The place of these metals in the steel industry has already been discussed.

514. Tungsten is a white metal which is used in making high-speed steels. It has a very high melting point (about 3000° C.) and makes an excellent metal for the filaments of incandescent electric lamps. The metal can be drawn into exceedingly fine wires, which are very strong. Tungsten lamps use only about one-third as much current as the old carbon-filament lamps. The metal is replacing platinum for electrical contact points in automobile vibrators.

SUMMARY OF CHAPTER XXXVIII

GOLD is found free and is obtained from the surrounding rock by mechanical separation, by the amalgamation process, or by the cyanide process. Gold is a heavy, soft, malleable metal. It is usually alloyed with copper to increase its wearing power. It is insoluble in most reagents but will dissolve in aqua regia, forming chlorauric acid.

PLATINUM occurs native, alloyed with similar metals. It is a very heavy, high-melting metal which is attacked by very few chemicals. It dissolves in aqua regia, forming chloroplatinic acid. Finely divided platinum is an excellent catalyst for gas reactions.

MANGANESE forms a number of series of compounds, in which it has different valences. Manganese dioxide (pyro-

lusite) is found naturally. The permanganates are strong oxidizing agents.

CHROMIUM forms two oxides: Cr_2O_3, which is basic, and CrO_3, which is acidic. The former corresponds to the chromic salts, the latter to chromic acid. The chromates and dichromates are strong oxidizing agents.

TUNGSTEN, MOLYBDENUM, AND VANADIUM in the form of their iron-alloys are used in the manufacture of special steels. *Lamp filaments* are made of tungsten.

Questions and Problems

1. The first metals known to have been used by the human race were gold and silver. Give the reason.

2. Write the equation for the decomposition of chloroplatinic acid by heat.

3. What precautions must be taken in the use of platinum vessels?

4. Gold coins are 90% gold and 10% copper. Express this in carats.

5. What reaction did we catalyze with manganese dioxide?

6. Write the equation for the oxidation of hydrochloric acid by potassium permanganate.

7. In what way is platinum better than gold for laboratory crucibles?

8. What properties has tungsten which fit it for use as a filament in electric lamps?

9. Which are the more stable, manganates or permanganates?

10. What is the difference in composition and properties between potassium chromate and potassium dichromate?

11. Write the equation for the oxidation of hydrochloric acid by sodium chromate.

12. If 4.10 grams of platinum are dissolved in aqua regia, how many grams of chloroplatinic acid (H_2PtCl_6) are obtained?

13. How many cubic centimeters of hydrogen (standard conditions) can be obtained from 50 cc. of hydrochloric acid (Sp. Gr. 1.1) containing 20% HCl reacting with an excess of metallic manganese?

14. How many grams of aluminum powder must be used in the Goldschmidt process to obtain all the chromium from a kilogram of chromic oxide (Cr_2O_3)?

15. How many pounds of potassium permanganate ($KMnO_4$) could be prepared from 100 pounds of pyrolusite? Assume that all the manganese in the ore is used and that the ore is 85% manganese dioxide (MnO_2).

Topic for Further Study

Rare elements in industry. Recent developments have shown that some rare elements which were thought to be only of scientific interest have properties which make them of the greatest industrial importance. The scientific study of these substances has thus been well rewarded. What rare elements are commercially important? For what is each used? (Slosson's *Creative Chemistry* and Duncan's *Chemistry of Commerce.*)

CHAPTER XXXIX

RADIUM AND RADIOACTIVITY

Radioactivity — radium — radium emanation, radon — disintegration series — radioactive elements and the periodic table — disintegration of atomic nucleus — possible unity of matter — transmutation of elements — uses of radium — radium and the atomic theory.

515. Radioactivity. It has been found that a number of chemical elements give off peculiar radiations which have much the same effect as the X ray; that is, they will penetrate such materials as black paper, affect a photographic plate, discharge an electroscope, and cause fluorescence in certain minerals. These effects were first discovered in 1896 by Becquerel, a French scientist, as he was examining a crystal of a salt of the element **uranium.** The general phenomenon was called **radioactivity.** Pierre Curie and his wife (Fig. 259), starting with this discovery, were able to isolate two or three other elements which were much more radio-

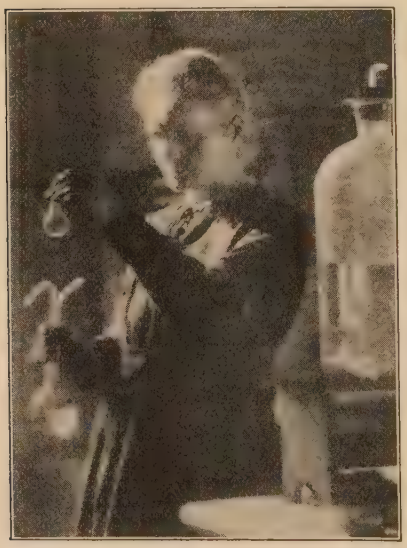

Fig. 259. Marie Sklodowska Curie (1867–). Professor of physics at the Sorbonne, University of Paris.

active than uranium. The first of these to be obtained was **polonium**; but radium was found in larger quantities and is the most important.

Radium is present in very minute amounts in **pitch blende** (an impure uranium oxide); only one gram of it can be obtained from every three tons of rock. As might be imagined, the separation of this element involves a difficult, complicated, and laborious chemical process.

516. Radium. Radium is a metal which chemically closely resembles barium and is in fact the next element below it in the periodic table. A number of its salts and the free metal itself have been prepared, and from their *purely chemical properties* there is little to distinguish the element from the rest of the calcium family.

Radium and all its salts are, however, extremely radioactive. This property is quite independent of the nature of the salts and is as apparent in radium bromide as in the free metal. In fact, what is sometimes spoken of as "radium" is in reality the salt radium bromide; it is the common form in which the element is kept and used. *Radioactivity thus seems to be a property of the radium atom* and to be independent of its chemical combination. The extreme radioactivity of radium and its salts can be shown by the effect on a photographic plate, by the discharge of an electroscope, or by a fluorescent screen.

517. Three kinds of rays from radium. It has been found that radium salts are actually giving off *three kinds of so-called rays*, which differ widely in their penetrating power and in the way in which they are affected by a magnetic field. The experiment shown in figure 260 illustrates the effect of the magnetic field on radium rays. Those called

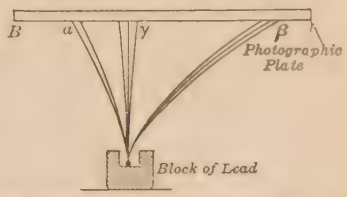

Fig. 260. Effect of a magnetic field on rays emitted by radioactive substances.

the **alpha** (α) **rays** have very little penetrating power and are found to be positively charged particles. The **beta** (β) **rays** are much more penetrating and are, in fact, merely a stream of electrons, exactly like those found in the vacuum tube. The **gamma** (γ) **rays** are not affected by a magnetic field and are nothing but the X rays which are produced by the action of the beta rays on some of the solid material through which they pass. It is these gamma, or X, rays which give to radium the extreme radioactivity which was first noticed.

518. Energy of radium. Another very surprising property of radium and its salts is that *the nature and amount of its radioactivity are entirely independent of the temperature* and of any other known conditions. The chemist has been unable to modify in any way the radioactivity of radium. It is as strong in liquid air as it is at the highest temperature. This is very unlike usual chemical reactions, which are always greatly affected by the temperature.

There is still another remarkable property of radium salts: *they are continually producing heat* and are generally three to five degrees warmer than the surrounding atmosphere. The amount of heat evolved has been measured and found to be such that one gram of radium salt gives off 100 calories per hour. This constant evolution of heat apparently goes on indefinitely. But, as a matter of fact, we shall see later that this is not the case, that radium is gradually disappearing, and that at the end of 2000 years it will be half gone. Thus, radium is not a source of perpetual energy, as is sometimes stated.

519. Radium emanation, radon. We have seen that the beta rays are a stream of electrons. The *alpha rays have been shown to be positively charged* ***helium*** *atoms*. This very remarkable fact has repeatedly been proved by collecting enough of these " rays " to produce the characteristic spectrum of helium.

We can obtain from radium another gas, which was first known as **radium emanation** but is now called **radon** (sometimes

niton). This gas is continuously being given off by radium compounds and can be pumped away from radium salts and obtained quite pure. **Radon** is clearly a definite element and finds a place in the periodic system as the last member of the family of rare gases. It is chemically inert, is monatomic, and has the molecular weight 222, exactly four units less than the atomic weight of radium. We thus see that from radium we have obtained two definite elements, one a known element, helium, and the other **radon.** The formation of helium and radon proceeds continuously in all radium compounds. This must be due to a disintegration of the radium atom itself; hence we have here the atom of one element actually being transformed into the atoms of two other elements. The atomic weight of radon is in this connection significant. It is exactly the difference between the atomic weights of radium and helium. *This disintegration of the radium atom the chemist cannot in any way modify or control.* He can merely observe it. Therefore, we cannot say that the chemist is able to change radium into helium and radon, but rather that the radium atom itself breaks down into these elements in spite of all that the chemist may do.

520. The disintegration series. The beta rays which are given off by a sample of radium salt are not a part of the decomposition of radium into radium emanation, but are the result of later changes. Radium emanation itself goes into another element, a solid called **radium A,** at the same time producing another alpha particle (a charged helium atom). **Radium A** disintegrates, forming successively radium B, C, D, E, and F. When radium F breaks up, it forms an element, radium G, whose atomic weight is 206. In each case the change is attended by the production of an electron or an alpha particle. The electrons emitted in the later stages of the disintegration of the radium atom are the beta rays which are given off by a sample of radium salt.

It will be noticed that the last product of the change is radium G; this is no longer radioactive, because it undergoes no further changes and gives off no charged particles. This substance shows all the chemical properties of ordinary lead and cannot be distinguished from the latter except that *it has a lower atomic weight*, and a different density. In other words, radium G is an *isotope* of ordinary lead.

An examination of the lead formed in radioactive ores (that is, ores which contain radium) showed that it had an atomic weight and density different from ordinary lead. This lead (radium G) was probably formed in that particular ore by the disintegration of the radium atoms. *The experimental demonstration of the existence of two kinds of lead, identical in chemical properties and X-ray spectra but different in properties involving atomic mass, was the first proof of the existence of isotopes.*

Every expulsion of a helium atom in the form of an alpha particle should lower the atomic weight of the element by four units (the atomic weight of helium). There are five such changes between radium and radium G, the end point. Subtracting these twenty units (5×4) from the atomic weight of radium (226) gives 206 for the atomic weight of radium G. The experimentally determined atomic weight of lead from pure radium ore is almost exactly 206 as compared with 207.2 for ordinary lead. That this "lead" is really radium G seems established beyond doubt, and our general picture of the radium disintegration is complete.

521. Radioactive elements and the periodic table. The accompanying diagram shows the position in the periodic table of the various disintegration products of radium. The position of these elements has been determined by their X-ray spectra, and is verified by their chemical properties. It will be noted that in group 4 there are 3 elements which are isotopes of ordinary lead; two of these, radium B and radium D, are radioactive; the other, radium G, is inactive, as explained above. Simi-

LAST TWO ROWS OF THE PERIODIC TABLE SHOWING POSITION OF THE DISINTEGRATION PRODUCTS OF RADIUM

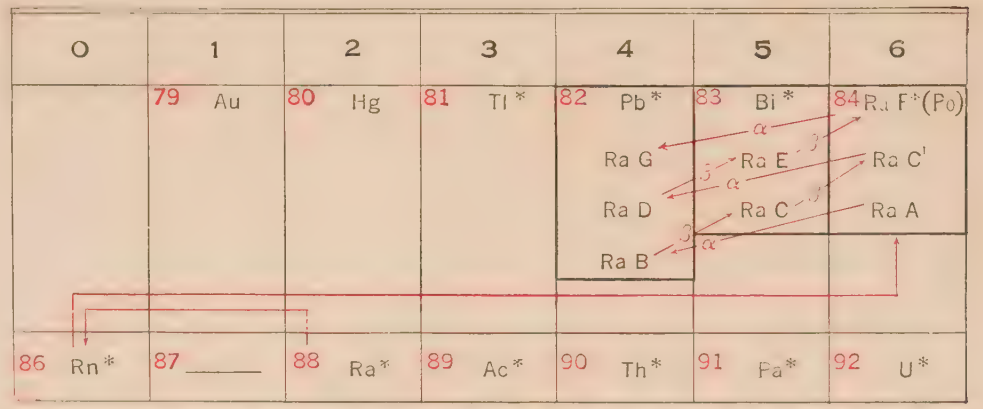

Fig. 261. The positions marked by a star (*) are occupied not only by the elements given but by the disintegration products of the Thorium and Uranium series. Note that in the change from Rn (radon) to Ra A, the change from the zero group of one row to the sixth group of the *higher* row is equivalent to moving two positions to the left in the same row (α change). Radium F is also called Polonium (Po).

larly in group 5 we have two radioactive elements, which are isotopes of ordinary bismuth.

There are other disintegration series besides the radium series. Thorium seems to be the starting point of a series of radioactive elements. Probably radium itself has been slowly formed as a product of the radioactive disintegration of uranium, and so is really not the starting point but the middle of a series. The elements formed in the thorium and uranium series occupy positions in the periodic series indicated by a star in the diagram (Fig. 261).

522. The disintegration of the atomic nucleus. The most probable explanation of radioactive disintegration is to be found in terms of the modern ideas concerning the structure of matter. We have already seen (§ 325) that we can picture an atom as made up of a positive nucleus surrounded by rings of electrons. The disintegration of radioactive elements appears to be a disintegration of the nucleus. Thus, when a radioactive element disintegrates, either an electron (a beta particle) is shot from *within the nucleus* or a doubly charged helium atom (an alpha particle) from the same source; or both changes may occur. The loss of one electron *from the nucleus* increases the net positive charge (the atomic number) by one; the newly formed element therefore belongs in the next place to the *right* in the periodic table. On the other hand, the loss of a doubly positively charged helium atom decreases the net nucleus charge by two, and the new element is to be placed two groups to the *left*. If two electrons and one alpha particle are emitted, the new element has the same nuclear charge and the same atomic number, and is isotopic with its parent. The accompanying diagram illustrates some of these changes. They have been followed by physical measurements of the characteristic radiations emitted by the elements during the disintegration. In many cases the life of one of the elements is so short that it is half disintegrated in a few minutes; in almost all cases the

amounts of the substances involved have been too small to see or even weigh. The results are nevertheless beyond dispute, thanks to the accuracy of the physical methods of measuring the characteristics of the electrons and alpha particles shot off from these spontaneously exploding nuclei.

This nuclear decomposition of the radioactive elements, it must always be remembered, does not involve any of the electrons *outside* the nucleus. These electrons merely rearrange themselves in the newly formed element to correspond to the positive charge on the nucleus. The chemical properties of a certain element which depends on the arrangement of these electrons (particularly the outer, or valence, electrons) are the same, whether the element be formed as a result of radioactive change or not. This has already been mentioned in the case of the leads, which, being end-products of radioactive changes, are themselves inactive; and their differences can be detected only by atomic weight or density determinations.

523. The possible unity of all matter. Radioactive changes establish the fact that certain atoms can break down forming new elements, helium atoms and electrons. If the nucleus of the atom is involved in these changes, the nucleus itself must be a complicated structure containing both electrons and positively charged helium atoms. It has been suggested that the nuclei of all atoms are built out of positively charged hydrogen atoms, called **protons,** and electrons. In radioactive changes one would have to assume that four protons and two of the nuclear electrons went off together as the doubly charged helium atom whenever an alpha particle was emitted.

It is evident that if all elements are built out of protons and electrons (some in the nucleus, some outside), the atomic weights should be practically whole numbers, since the atomic weight of hydrogen is nearly one, and the mass of the electron is negligible. The actually determined atomic weights of many elements are far from whole numbers. Aston has shown that this

is merely because the elements as we know them are mixtures of isotopes (§ 224). The atomic weights of the various isotopes are as nearly whole numbers as can be determined. Therefore there is little difficulty in imagining that each isotope is built out of hydrogen nuclei and electrons.

The present picture of the structure of matter according to this theory may be summarized by considering the element chlorine, which has two isotopes of atomic weight 35 and 37. Each has the atomic number 17; that is, there are 17 electrons outside the nucleus arranged in groups as follows: 2, 8, 7. The nucleus has a positive charge of 7. This is a *net* positive charge and might result from many combinations of nuclear electrons and protons. For the isotope of atomic weight 35, we imagine that there are 35 protons (giving a plus charge of 35) and 18 nuclear electrons. The difference (+ 35 − 18) is the atomic number 17. Similarly, for the isotope of weight 37, there must be 37 protons and 20 nuclear electrons, the atomic number being as before; the mass of the nucleus and thus the atomic weight are, however, different (Fig. 262).

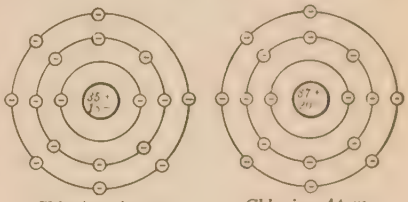

Fig. 262. Isotopes of chlorine.

524. The transmutation of elements. The idea that the nuclei of all atoms are composite at once suggests the possibility of breaking down complex atoms into simpler ones — a transmutation of elements. Such a process is going on all the time in the case of radioactive elements; but we know of no method to hasten or retard it. An English physicist, Rutherford (Fig. 263), performed some experiments in which he obtained evidence that nitrogen atoms, when bombarded by alpha particles, formed some hydrogen atoms. The amounts of matter changed

were so small that the hydrogen atoms could not be detected by chemical methods but only by physical measurements. Rutherford's experiments are the only definitely established case of what might be termed artificial disintegration. Possibly someone in the future will find a method of bringing about similar changes by means of powerful electric currents or forces other than those furnished by the alpha particle when it is shot from the exploding radium nucleus.

Fig. 263. Sir Ernest Rutherford (1871–). Professor of Physics at Cambridge University, England. Made clear the nature and source of the rays evolved during radioactive transformations.

525. Uses of radium. The radiations given off by radium (in particular the beta rays and their secondary product, the gamma rays) are extremely active. It is possible, with their aid, to take pictures in exactly the same way as with the X rays generated by an electric current in a vacuum tube. Radium rays exert a very powerful action on all living matter, and it has been thought that they would be useful in curing various diseases. The results have not been so successful as was first hoped; but in treating certain kinds of cancer and similar growths, radium seems to be very beneficial. Radium is extremely expensive, one gram costing about $150,000. It is, however, continually producing radium emanation; and the emanation instead of the radium itself is often used in treating diseases. Every day the emanation can be pumped off from the radium salt and collected in very tiny

glass tubes (Fig. 264). These tubes can then be inserted in the flesh near the cancer. The radium emanation in the tube goes through the complete series of changes, ending finally as radium G and producing alpha, beta, and gamma rays. The

Fig. 264. Apparatus in the Warren Laboratory of Bio-Physics (Boston) for pumping radium emanation from the radium, which is in the vault.

curative power rests in the action of these rays on the diseased tissue.

Certain radioactive elements in an impure condition have been used in the manufacture of luminescent paint. They are mixed with zinc sulfide, which, as we have seen, fluoresces when the rays from radium strike it.

SUMMARY OF CHAPTER XXXIX

CERTAIN MINERALS GIVE OFF RADIATIONS LIKE X RAYS and are called radioactive. The element radium, isolated in very small amounts from an ore of uranium, is extremely radioactive.

RADIUM is chemically much like barium. Its radioactivity is independent of the chemical combination of the element. The bromide is generally used.

RADIUM GIVES OFF THREE SORTS OF " RAYS ": *alpha* particles, which are charged helium atoms; *beta* rays, or *electrons;* and *gamma* rays, which are X rays produced by the *electrons.*

RADIUM EVOLVES HEAT slowly but continuously. It produces a new element called radium emanation, or *radon,* which is a rare gas. The disintegration of the radium atom into a helium atom and a radon atom goes on continuously and cannot be in any way controlled or altered. Radon also disintegrates, and there is a whole series of disintegration products from radium. The final form is radium G. Radium G is chemically like ordinary lead but has a different atomic weight. These two kinds of lead are *isotopes.*

OUR ATOMIC THEORY HAS BEEN GREATLY EXTENDED by the study of radioactive substances. Atoms of radioactive elements are for some reason unstable and explode, expelling either electrons or atoms of helium, or both. The atoms of most of the elements are stable and are probably made up of a positive nucleus and a number of electrons revolving about the nucleus.

RADIUM IS USED in medicine for treating cancer. Certain impure radioactive elements are used in making luminescent paints.

Questions

1. How is radioactivity different from the usual chemical action?

2. Why was it formerly thought that radioactivity contradicted the Law of Conservation of Energy?

3. What are the chief natural sources of radium?

4. What is meant by saying that uranium is the " parent " element and lead is the " end product " of a series of radioactive elements?

5. What important changes in our theory of atoms have been brought about by the experiments with radium?

6. Why is radium such a very costly metal?

7. What are the distinguishing properties of the alpha, beta, and gamma radiations sent off by radium?

8. How could you tell whether a substance was radioactive?

9. How could you test the activity of a radioactive substance?

10. What is the most striking difference between radium and barium?

11. What are isotopes? Illustrate with radioactive elements.

12. Describe the process of "transmutation of the elements" in terms of the modern theory of atomic structure.

Topics For Further Study

Modern alchemy. The alchemists of old endeavored to transform one element into another; they failed. To-day chemists can watch one element spontaneously change into another, but they can neither hasten nor retard the transmutation. How does "modern alchemy" differ from the old? (Martin's *Modern Chemistry*, Russell's *ABC of Atoms*, and Tilden's *Chemical Discovery*.)

Review Questions

1. Mention one useful property of each of the following, and give in each case one useful application based upon that property: (*a*) HgCl, (*b*) $HgCl_2$, (*c*) $AgNO_3$, (*d*) Pb_3O_4, (*e*) $CuSO_4$.

2. Write equations for the following reactions:
(*a*) silver nitrate (solution) and zinc
(*b*) silver nitrate and potassium bromide
(*c*) silver and hot concentrated sulfuric acid
(*d*) silicon dioxide and fused sodium carbonate
(*e*) ethyl alcohol burned completely in oxygen

3. What weight of silver nitrate ($AgNO_3$) reacts with 7.3 grams of crystallized calcium chloride ($CaCl_2 \cdot 6\,H_2O$) to precipitate all the chlorine as silver chloride?

4. Describe briefly the refining of copper. How does ordinary copper compare in purity with other metals as commercially supplied?

5. In a photographic dry plate, what is the substance sensitive to light; what function does the developer perform; and what is meant by "fixing"?

APPENDIX

CERTAIN PHYSICAL PRINCIPLES IN REGARD TO GASES

Standard conditions for gases. The **density** of any substance is the *weight of a unit volume;* that is, the number of grams per cubic centimeter or per liter. But in determining the density of a gas, such as air, oxygen, or hydrogen, we have a rather difficult problem. This is because gases are all very light and therefore hard to weigh, and also because a gas has no definite volume since it always fills the containing vessel. Then, too, the volume of gases is very much influenced by the temperature and pressure to which they are subjected. We must weigh a given volume of a gas under known conditions of temperature and pressure, and then compute what the volume would be under standard conditions. Chemists have generally agreed that **zero degrees centigrade** (0° C.) and 760 **millimeters** (mm.) **pressure** *shall be considered the standard, or normal, temperature and pressure for gases.* We shall not endeavor to measure gases at 0° C. (the temperature of melting ice) and 760 mm. (the average pressure of the atmosphere at sea level); but knowing the actual temperature and pressure, we shall calculate what the volume of the gas would be under these standard conditions.

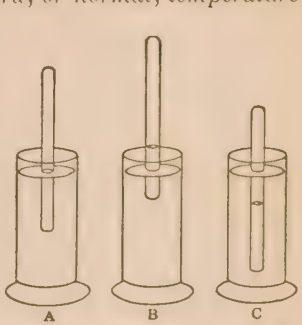

Fig. 265. Differences of level affect volume of gas.

Measurement of atmospheric pressure. Since we usually collect gases over water in a pneumatic trough and make the level of the water inside the measuring jar or bottle the same as that of the water outside (Fig. 265 A), we

are subjecting the gas to atmospheric pressure. To measure the pressure of the atmosphere, we read the barometer. The mercurial barometer (Fig. 266) consists of a column of mercury which just balances the pressure of the atmosphere. Usually the instrument consists of a stout glass tube about a meter long, closed at one end. This has been completely filled with mercury and then inverted so that the open end projects into a cup or reservoir of mercury. At sea level the mercury in the tube sinks to a level about 760 millimeters above the mercury surface in the cup. The space above the mercury in the tube is empty, except for a minute quantity of mercury vapor; in fact, it is the most perfect vacuum that we know how to make. To "read the barometer" means simply to measure accurately the height of the mercury column above the surface of the liquid in the reservoir. Such a barometer indicates the variations in atmospheric pressure from day to day due to fluctuations in the atmosphere itself; it also indicates changes of pressure due to changes in the elevation of the observer.

Fig. 266. Mercurial barometer for measuring atmospheric pressure.

The volume of a gas changes with pressure. This was first investigated in the case of air by Robert Boyle (1626–1691). The results of his experiments showed that if we start with a given volume of air subjected to a certain pressure and then double the pressure, the volume of air will be reduced to one-half (Fig. 267). If the pressure is made three times as great, the volume of the air will be reduced to one-third, provided the temperature of the air is kept constant. This was found to be a general principle which applies to all gases. It is known as BOYLE'S

LAW and may be stated as follows: *The volume of a given weight of a gas at constant temperature varies inversely as the pressure.*

This may also be expressed in symbols, thus:

$$\frac{V}{V'} = \frac{P'}{P}$$

or
$$PV = P'V' \qquad \text{(I)}$$

where V and P denote the volume and pressure of a given weight of gas at some temperature, and V' the volume under a different pressure P' but at the same temperature.

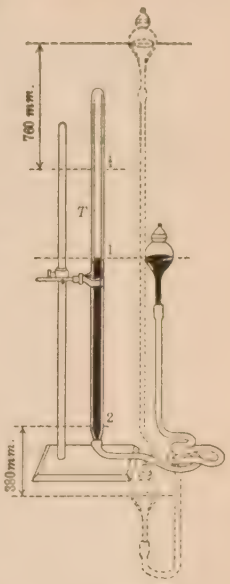

Fig. 267. Apparatus for illustrating Boyle's Law. Pressure is varied by raising and lowering mercury reservoir.

FOR EXAMPLE, suppose a certain weight of oxygen has a volume of 1200 cc. measured at 740 mm. What will be the volume under standard pressure (760 mm.) if the temperature remains constant?

According to Boyle's Law

$$PV = P'V'$$

Substituting the values given in the problem, we have

$$760\ V = 740 \times 1200$$

or
$$V = \frac{740 \times 1200}{760} = 1169 \text{ cc.}$$

It will serve as a useful check on this result to note that the gas under standard pressure will be subjected to a greater pressure than before, and accordingly its volume will be less.

NOTE. In solving such problems in chemistry it will save much time to use a four-place logarithmic table, or, better still, a slide rule. Generally it is sufficiently accurate to get three significant figures (§ 127) in the answer.

PROBLEMS

1. What will be the volume of 45 cc. of hydrogen when its pressure changes from 770 mm. to 750 mm.? Assume no change in temperature.

2. If 380 cc. of oxygen were measured at 15° C. and at 745 mm. pressure, what would be the volume at 760 mm., and at the same temperature?

3. A gas under a pressure of 60 cm. and at 20° C. has a volume of 645 cc. What will be its volume under a pressure of 80 cm. and at 20° C.?

4. If a certain quantity of gas under standard pressure (760 mm.) occupies 950 cc., find what volume it would occupy when subjected to a pressure of 77 cm. if the temperature were kept constant.

5. Oxygen is sold in steel cylinders under a pressure of 150 pounds per square inch. As the gas is used, the pressure drops. When it has dropped to 30 pounds, what fractional part of the original gas remains?

The volume of a gas changes with the temperature. We all know that nearly everything expands when heated. For example, the mercury or alcohol in a thermometer expands and so rises in the stem when warmed. But perhaps we are not familiar with the fact that gases when warmed expand much more than liquids; thus, air expands about nine times as much as water. Even more remarkable, however, is the fact that all gases expand at nearly the same rate.

Fig. 268. Tube containing dry air and a pellet of mercury.

It is easy to measure in a rough way the amount which gases expand (Fig. 268). If in the experiment we had begun with a volume of air of 273 cc. at 0° C. and had cooled the gas from 0° C. to − 1° C., the volume would have been reduced to 272 cc.; and if we had cooled it to − 10° C., the volume of the air would have become 263 cc. If, then, the air continued to contract at the same rate when cooled indefinitely, the volume of the air at − 273° C. would become zero. As a matter of fact, we can never get a gas to so low a temperature as − 273° C., because every known gas turns into a liquid before that temperature is reached. This temperature − 273° C. is, however, one of unusual interest in the study of

gases. It is called the **absolute zero,** and temperatures measured from this point as zero are called **absolute temperatures.** Absolute temperatures may be designated by the letter A. Thus, 0° C. is 273° A., 50° C. is 323° A., and 100° C. is 373° A. To change any temperature from the centigrade to the absolute scale, we have merely to add 273 degrees (Fig. 269).

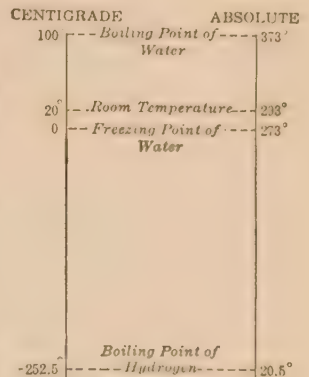

Fig. 269. Centigrade and absolute temperature scales.

The Law of Charles. The peculiar interest which this new thermometer scale has for the chemist lies in the fact that *the volumes which a given weight of gas occupies at two different temperatures are directly proportional to the absolute temperatures when the pressure is kept constant.* This is known as the LAW OF CHARLES.

This relation between the volume and temperature of a gas can be very concisely expressed algebraically:

$$\frac{V}{V'} = \frac{T}{T'} \qquad \text{(II)}$$

where V and V' represent the volumes of a certain quantity of gas at the same pressure but at different absolute temperatures, T and T'. If t is the temperature on the centigrade scale when the volume is V, then $T = 273 + t$; similarly, $T' = 273 + t'$.

FOR EXAMPLE, suppose we have a quantity of gas which measures 320 cc. when the temperature is 15° C. What volume will this occupy at 0° C., provided the pressure is kept constant?

First change the centigrade temperatures given in the problem to absolute temperatures by adding 273 and then substitute in the equation for the Law of Charles:

$$\frac{V}{320} = \frac{273}{273 + 15}$$

or $$V = \frac{320 \times 273}{288} = \mathbf{303\ cc.}$$

NOTE. In solving such problems the student would do well to compare his result with the original volume to see whether it is reasonable. If the temperature of a gas measured in the laboratory is 20° C., then the gas under standard conditions would contract about 7 per cent.

PROBLEMS

1. What volume would 160 cc. of oxygen, measured at 17° C., occupy at 0° C., if we assume that the pressure remains fixed?

2. If 250 cc. of gas are measured at − 10° C. and at 760 mm. pressure, what will be the volume under standard conditions?

3. A quantity of gas occupies 100 cc. when measured at 0° C. What will it measure when heated to 30° C. with the pressure kept constant?

4. Given 560 cc. of hydrogen measured at 10° C. If the gas is heated until its volume becomes 1000 cc., what will be its temperature on the centigrade scale, provided the pressure does not change?

5. What change in volume would occur if 2 liters of gas at 200° C. were cooled to 0° C., if we assume no change in pressure?

The gas equation. In practice the chemist usually has to make corrections for *both* the pressure and the temperature in reducing his volume of gas to standard conditions. It will therefore be helpful to combine the Laws of Boyle and Charles into one equation:

$$\frac{PV}{T} = \frac{P'V'}{T'} \qquad \textbf{(III)}$$

It will readily be seen that this equation reduces to equation I (Boyle's Law) when $T = T'$, and that if $P = P'$ the equation becomes $V/T = V'/T'$, which is another form of equation II (Charles' Law). Equation III is called the **gas equation.***

FOR EXAMPLE, suppose we wish to find the volume of a certain quantity of gas under standard conditions, that is, at 0° C. and 760

* There are certain deviations from these gas laws whose discussion is beyond the scope of this book. Only ideal gases follow the laws as discussed above.

mm. pressure, when it is known to occupy 1200 cc. at 15° C. and under a pressure of 740 mm.

Substituting in equation III we have

$$\frac{740 \times 1200}{273 + 15} = \frac{760 \times V'}{273 + 0}$$

whence

$$V' = \frac{740 \times 1200 \times 273}{760 \times 288} = 1100 \text{ cc.}$$

Correction for pressure of water vapor. When a gas is collected over water and the level of the water is the same within and without the measuring vessel, the inclosed gas is under atmospheric pressure. But to some extent water has evaporated into the vessel, and a part of the volume inclosed is due to the water vapor and not to the gas. This water vapor exerts a certain pressure, depending on the temperature. As the temperature rises, the pressure of water vapor increases steadily, as shown in the table in the Appendix.

The pressure inside a bottle of gas collected over water is the pressure of the gas *plus* the pressure of the water vapor, and is equal to that outside, which is simply atmospheric pressure. What we want, however, is merely the pressure exerted by the gas collected. Since we cannot easily remove the water vapor, we can do what amounts to the same thing. *We subtract the pressure of the water vapor* (aqueous tension), *expressed in millimeters of mercury, from the barometric pressure*, and the result is the pressure of the dry gas, or the **corrected pressure.** This we use in our calculation.

NOTE. A table in the Appendix gives the pressures due to water vapor at various temperatures.

FOR EXAMPLE, suppose a gas measured 300 cc. over water when the barometer read 740 mm. and the temperature was 25° C. What would be its volume under standard conditions?

From the table for aqueous tension we see that the pressure of water vapor at 25° C. is 24 mm.; therefore the corrected pressure is 740–24 or 716 mm.

Substituting in the gas equation, we have

$$\frac{716 \times 300}{298} = \frac{760 \times V'}{273}$$

whence $$V' = \frac{716}{760} \times \frac{273}{298} \times 300 = \mathbf{259\ cc.}$$

Correction for difference in level. We have assumed that the gases were collected over mercury or water in bottles, and that the level of the liquid was the same outside and inside the tube. Occasionally it is impossible to arrange the apparatus in this way, and then we must make a correction for the difference of level. When the level of the liquid inside the tube is lower than that outside (Fig. 265 c), then the pressure is greater than atmospheric; and when the inside level is higher (Fig. 265 B), then the pressure is less than atmospheric. If the liquid is mercury, the difference in levels is added to or subtracted from the height of the barometer. Since water is about one-thirteenth as heavy as mercury, the correction for a difference in level for water is only one-thirteenth as much as for mercury.

EXAMPLE. Suppose 210 cc. of gas were collected over water in a bottle in which the water level was 8.0 cm. above that in the trough outside and the temperature was 22° C. and the barometer read 764 mm. Find the corrected volume under standard conditions.

SOLUTION. From the Table in the Appendix, we find that the pressure of water vapor at 22° C. is approximately 20 mm. Therefore the corrected pressure is:

$$764 - \underset{\text{water vapor}}{20} - \underset{\text{diff. in level}}{\frac{80}{13}} = 738 \text{ mm.}$$

In making these corrections we take the nearest whole number of millimeters, because this error is generally less than that involved in reading the barometer or the volume.

Then substituting in the gas equation, we have

$$\frac{738 \times 210}{295} = \frac{760 \times V'}{273}$$

$$V' = \frac{738}{760} \times \frac{273}{295} \times 210 = \mathbf{189\ cc.}$$

CHECK: It will be seen that the pressure reduced the volume about 3% and the temperature about 7%; and therefore *both* temperature and pressure reduce the volume about 10%.

PROBLEMS

1. A volume of dry gas measures 1050 cc. at 740 mm. and 22° C. What would be its volume under standard conditions?

2. A quantity of hydrogen and water vapor standing over water in a measuring tube has a volume of 45.3 cc. The temperature is 22° C.; the barometer reads 738 mm. Correct the volume of hydrogen to standard conditions.

3. Ten liters of gas stand over water at 20° C. with the barometer reading 75 cm. The gas is passed through a drying agent and collected over mercury. If the temperature and barometric pressure remain constant, what will be its volume?

4. A volume of nitrogen standing over water in a tube with levels the same inside and outside measures 80 cc. The temperature is 24° C., and the barometer stands at 770 mm. Find the volume under standard conditions.

5. The volume of a gas collected over mercury is 40 cc. when the level inside the tube is 80 mm. below that outside, the temperature is 18° C., and the barometer stands at 745 mm. Find the volume at standard conditions.

6. Hydrogen was collected over water in a graduated cylinder. The volume was 180 cc. when the water level inside was 10 cm. above that outside, the temperature was 15° C., and the barometer stood at 750 mm. Find the corrected volume under standard conditions.

7. A flask holding a liter of air was sealed at 20° C. and heated to 200° C. Assuming the original pressure of the air to be 15 pounds per square inch, find the pressure of the air (pounds per square inch) in the flask. (The volume of the flask may be considered as unchanged.)

8. A cylinder of compressed gas holds 40 liters at a pressure of 30 atmospheres and at 27° C. The cylinder breaks in a room where the pressure is one atmosphere and the temperature is 17° C. What is the volume of the expanded gas?

9. A certain quantity of oxygen measures 40 cc. when the pressure is 765 mm. and the temperature is 15° C. What will be its volume when the pressure is 740 mm. and the temperature is 25° C.?

10. Twenty cubic centimeters of hydrogen is contained in a measuring tube in which the level of the water is 39 mm. above the outside level; find the corrected pressure. Assume that the barometer stands at 740 mm., and the temperature is 21° C.

LIST OF BOOKS FOR FURTHER STUDY

ABC of Atoms — Bertrand Russell. E. P. Dutton and Co.

Chemical Discovery and Invention in the Twentieth Century — Sir William A. Tilden. E. P. Dutton and Co.

Chemistry in Agriculture — edited by J. S. Chamberlain. The Chemical Foundation, Inc.

Chemistry in America — E. F. Smith. D. Appleton and Company.

Chemistry in Industry, 2 volumes — edited by H. E. Howe. The Chemical Foundation, Inc.

Chemistry in the Service of Man — Alex. Findlay. Longmans, Green, and Co.

Chemistry in the World's Work — H. E. Howe. D. Van Nostrand Co.

Chemistry of Commerce — R. K. Duncan. Harper & Brothers.

Creative Chemistry — Edwin E. Slosson. The Century Co.

Discoveries and Inventions of the Twentieth Century — Edward Cressy. E. P. Dutton and Co.

Essays in Historical Chemistry — E. Thorpe. The Macmillan Co.

History of Chemistry — F. J. Moore. McGraw-Hill Book Co.

Modern Chemistry and its Wonders — G. Martin. D. Van Nostrand Company.

Non-Technical Chats on Iron and Steel — L. W. Spring. Frederick A. Stokes Company.

Outlines of Industrial Chemistry — F. H. Thorp and W. K. Lewis. The Macmillan Co.

Photography for Students of Physics and Chemistry — Louis Derr. The Macmillan Co.

Science Remaking the World — Otis W. Caldwell and Edwin E. Slosson. Doubleday, Page and Co.

SOLUBILITY OF SOLIDS IN WATER

This table shows the number of grams of anhydrous solid which when dissolved in 100 grams of water make a saturated solution at the temperature stated.

Substance	Formula	0° C.	10° C.	20° C.	100° C.
Ammonium chloride	NH_4Cl	29.4	33.3	37.2	77.3
Barium chloride	$BaCl_2$	31.6	33.3	35.7	58.8
Calcium hydroxide	$Ca(OH)_2$	0.185	0.176	0.165	0.077
Copper sulfate	$CuSO_4$	14.3	17.4	20.7	75.0
Potassium chloride	KCl	27.6	31.0	34.0	56.7
Potassium nitrate	KNO_3	13.3	20.9	32.0	246.
Sodium chloride	$NaCl$	35.7	35.8	36.0	39.0
Sugar	$C_{12}H_{22}O_{11}$	179.	190.	204.	487.

SOLUBILITY OF VARIOUS GASES IN WATER*

(At 15° C. and under 760 mm. pressure)

Name of Gas	Volume Absorbed by 1 Liter of Water
Very Soluble	
Ammonia	802. liters
Hydrogen chloride	458. "
Sulfur dioxide	47.3 "
Moderately Soluble	
Hydrogen sulfide	3.05 "
Chlorine	2.63 "
Carbon dioxide	1.02 "
Slightly Soluble	
Oxygen	0.034 "
Hydrogen	0.019 "
Nitrogen	0.018 "

*Taken from Kaye and Laby's *Physical and Chemical Constants*. Longmans, Green, and Co.

PRESSURE OF WATER VAPOR, OR AQUEOUS TENSION

(*In millimeters of mercury*)

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
0° C.	4.6 mm.	11° C.	9.8 mm.	22° C.	19.8 mm.
1°	4.9	12°	10.5	23°	21.0
2°	5.3	13°	11.2	24°	22.3
3°	5.7	14°	12.0	25°	23.7
4°	6.1	15°	12.8	26°	25.1
5°	6.5	16°	13.6	27°	26.7
6°	7.0	17°	14.5	28°	28.3
7°	7.5	18°	15.5	29°	29.9
8°	8.0	19°	16.5	30°	31.7
9°	8.6	20°	17.5	50°	92.3
10°	9.2	21°	18.6	100°	760.0

DENSITIES OF IMPORTANT GASES

(*Approximate weight of 1 liter under standard conditions*)

Acetylene (C_2H_2)	1.16 grams
Air	1.29 "
Ammonia (NH_3)	0.77 "
Carbon dioxide (CO_2)	1.98 "
Carbon monoxide (CO)	1.25 "
Chlorine (Cl_2)	3.17 "
Helium (He)	0.18 "
Hydrogen (H_2)	0.09 "
Hydrogen chloride (HCl)	1.64 "
Hydrogen sulfide (H_2S)	1.54 "
Methane (CH_4)	0.72 "
Nitric oxide (NO)	1.34 "
Nitrogen (N_2)	1.25 "
Nitrous oxide (N_2O)	1.98 "
Oxygen (O_2)	1.43 "
Sulfur dioxide (SO_2)	2.93 "

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TABLE OF ATOMIC NUMBERS AND ATOMIC WEIGHTS OF THE CHEMICAL ELEM

	SYMBOL	AT. NUMBER	AT. WEIGHT		SYMBOL	AT. NUMBER	A WE
Aluminum	Al	13	26.97	Mercury	Hg	80	200
Antimony	Sb	51	121.77	Molybdenum	Mo	42	96
Argon	A	18	39.91	Neodymium	Nd	60	144
Arsenic	As	33	74.96	Neon	Ne	10	20
Barium	Ba	56	137.37	Nickel	Ni	28	58
Beryllium	Be	4	9.02	Nitrogen	N	7	14
Bismuth	Bi	83	209.00	Osmium	Os	76	190
Boron	B	5	10.82	Oxygen	O	8	16
Bromine	Br	35	79.916	Palladium	Pd	46	106
Cadmium	Cd	48	112.41	Phosphorus	P	15	31
Calcium	Ca	20	40.07	Platinum	Pt	78	195
Carbon	C	6	12.000	Potassium	K	19	39
Cerium	Ce	58	140.25	Praseodymium	Pr	59	140
Cæsium	Cs	55	132.81	Radium	Ra	88	225
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhodium	Rh	45	102
Cobalt	Co	27	58.94	Rubidium	Rb	37	85
Columbium	Cb	41	93.1	Ruthenium	Ru	44	101
Copper	Cu	29	63.57	Samarium	Sm	62	150
Dysprosium	Dy	66	162.52	Scandium	Sc	21	45
Erbium	Er	68	167.7	Selenium	Se	34	79
Europium	Eu	63	152.0	Silicon	Si	14	28
Fluorine	F	9	19.00	Silver	Ag	47	107
Gadolinium	Gd	64	157.26	Sodium	Na	11	23
Gallium	Ga	31	69.72	Strontium	Sr	38	87
Germanium	Ge	32	72.60	Sulfur	S	16	32
Gold	Au	79	197.2	Tantalum	Ta	73	181
Hafnium	Hf	72	178.6	Tellurium	Te	52	127
Helium	He	2	4.000	Terbium	Tb	65	159
Holmium	Ho	67	163.5	Thallium	Tl	81	204
Hydrogen	H	1	1.008	Thorium	Th	90	232
Indium	In	49	114.8	Thulium	Tm	69	169
Iodine	I	53	126.932	Tin	Sn	50	119
Iridium	Ir	77	193.1	Titanium	Ti	22	47
Iron	Fe	26	55.84	Tungsten	W	74	184
Krypton	Kr	36	82.9	Uranium	U	92	238
Lanthanum	La	57	138.90	Vanadium	V	23	51
Lead	Pb	82	207.22	Xenon	Xe	54	130
Lithium	Li	3	6.940	Ytterbium	Yb	70	173
Lutecium	Lu	71	175.0	Yttrium	Y	39	89
Magnesium	Mg	12	24.32	Zinc	Zn	30	65
Manganese	Mn	25	54.93	Zirconium	Zr	40	91

TABLE OF THE MORE IMPORTANT ELEMENTS

with their symbols, approximate atomic weights, and valences

ent	Sym-bol	Approx. At. Wt.	Valence	Element	Sym-bol	Approx. At. Wt.	Valence
um .	Al	27	III	Manganese	Mn	55	II IV
. .	Ba	137	II	Mercury .	Hg	200	I II
e .	Br	80	I	Nickel . .	Ni	58.7	II
n .	Ca	40	II	Nitrogen .	N	14	III V
.	C	12	IV	Oxygen .	O	16	II
ie .	Cl	35.5	I	Phosphorus	P	31	III V
ium .	Cr	52	II III VI	Platinum .	Pt	195	IV
. .	Cu	63.6	I II	Potassium .	K	39	I
ie .	F	19	I	Radium .	Ra	226	II
. .	Au	197	I III	Silicon . .	Si	28	IV
n . .	He	4	——	Silver . .	Ag	108	I
gen .	H	1	I	Sodium .	Na	23	I
. .	I	127	I	Sulfur . .	S	32	II IV VI
. .	Fe	56	II III	Tin . . .	Sn	119	II IV
. .	Pb	207	II IV	Tungsten .	W	184	VI
esium	Mg	24	II	Zinc . . .	Zn	65	II

MON UNITS IN THE METRIC AND ENGLISH SYSTEMS

nillimeters = 1 centimeter (cm.) (mm.)
centimeters = 1 meter (m.)
cubic centimeters (cc.) = 1 liter (l.)
milligrams = 1 centigram (cg.) (mg.)
centigrams = 1 gram (g.)
grams = 1 kilogram (kg.)

1 cc. of water at 4° C. weighs 1 gram
2.54 centimeters = 1 inch
1 meter = 39.37 inches
1 liter = 1.06 quarts
1 gram = 15.4 grains
28.35 grams = 1 ounce
1 kilogram = 2.20 pounds
1 pint of water weighs about 1 pound